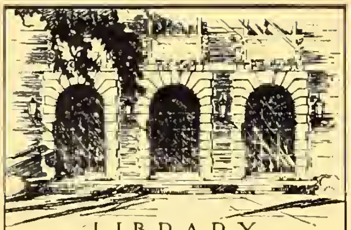

TABLE OF CONTENTS

1959-1960

TABLE OF CONTENTS

A STUDY OF THE KINETICS OF SOME REACTIONS OF $[Coen_2NH_3(OH_2)]^{3+}$ ION

Dean F. Martin September 29, 1959

I. INTRODUCTION

During the past twenty years, there has been an ever increasing interest in the mechanisms of inorganic reactions. The reactions of transition-metal complexes in solution have received special attention, and Basolo and Pearson[1] have written an excellent summary of the results of research in this area. Although much is known concerning the substitution and aquation reactions of complex compounds, detailed studies of cis-trans isomerization reactions are reported for but a few systems, e.g., $[Coen_2Cl_2]^+$, [2] $[Coen_2(OH_2)]^{3+}$, [3,4] $[Cr(C_2O_4)_2(OH_2)_2]^-$, [5,6] and $[Coen_2NCS(OH_2)]^{++}$ [7] ions.

The results of a recent study of the kinetics of the isomerization, racemization, and water-exchange reactions of $[Coen_2NH_3(OH_2)]^{3+}$ ion are reported here.

II. ISOMERIZATION OF trans-$Coen_2NH_3(OH_2)](NO_3)_3$.

The kinetics of the isomerization of trans-$[Coen_2NH_3(OH_2)](NO_3)_3$ in aqueous solution were followed spectrophotometrically over the temperature range 35-75°C. The rearrangement was found to be essentially complete. Under the conditions studied (temperature, pH, and ionic strength were maintained at constant values), the reaction followed pseudo-first-order kinetic law. At a given temperature, the kinetic data are summarized by the following relationship:

$$k_{obs} = k_{calc} = \frac{k_1 + \frac{k_2 K}{[H^+]}}{1 + \frac{K}{[H^+]}},$$

where k_{obs} and k_{calc} are, respectively, the observed and the calculated specific rate constants for the isomerization reaction; k_1 and k_2 are the "limiting" specific rate constants for the isomerization of trans-$[Coen_2NH_3(OH_2)]^{3+}$ and trans-$[Coen_2NH_3(OH)]^{2+}$ ions, respectively; and K is the calculated acid dissociation constant of trans-$[Coen_2NH_3(OH_2)]^{3+}$ ion.

III. RACEMIZATION OF cis-$[Coen_2NH_3(OH_2)](ClO_4)_3$.

Ingold and co-workers have noted(8) that changes either of geometrical or of optical configuration, i.e., isomerization or racemization, may be regarded as a manifestation of a single stereochemical mode of substitution, which they term "edge-displacement". It was therefore desirable to compare the rates of racemization and isomerization. With reaction conditions similar to those employed in the study of the trans-isomer, the kinetics of the racemization of cis-$[Coen_2NH_3(OH_2)]^{3+}$ ion were determined polarimetrically. It was found that the rate of racemization followed a pattern similar to that observed for the isomerization reaction.

IV. WATER-EXCHANGE OF $[Coen_2NH_3(OH_2)]^{3+}$ ION.

In order to elucidate the mechanism of the isomerization and racemization of $[Coen_2NH_3(OH_2)]^{3+}$ ion, the kinetics of the water-exchange reaction were studied using O^{16}-enriched water. The results of this study are not yet available, and the final postulation of the mechanism of the rearrangement reactions is best postponed.

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THE CHEMICAL EFFECTS OF NUCLEAR TRANSFORMATIONS

Jack G. Kay October 13, 1959

I. Introduction

In general, when a nuclear reaction occurs, the energy released appears immediately as kinetic and electronic energy of the reaction products. The chemical effects are results of reactions of the kinetically and electronically excited atoms or ions with the surrounding medium. Usually, the initial kinetic energy of an atom recoiling from a nuclear process is far in excess of chemical bond energies.

Willard (1) and McKay (2) have reviewed in general the reactions of energetic recoil atoms resulting from nuclear processes and Baulch and Duncan (3) have recently reviewed the quantitative aspects of such processes.

A large amount of work has been done in studies of the Szilard-Chalmers (4) process in which the radioactive isotopes produced by the (n,γ) reaction come to rest in a state that is not exchangeable with the state of the parent isotope, thus allowing the radioactive product to be easily separated from the parent. More recently, recoil reactions have been used as a means of synthesis of tritium-labeled organic molecules. (5)

The observations that recoil tritium and halogen atoms undergo substitution reactions in the gas phase have led to an investigation of whether recoil metal atoms would undergo similar substitutions. Accordingly, the reactions of Pb^{212} recoiling from alpha decay of Po^{216} in the presence of various hydrocarbons and other gases were studied.

II. Reactions of Recoil Lead in the Gas Phase (6)

The source of the Po^{216} for this study was the rare gas isotope, Rn^{220}, obtained by sweeping a solution of thorium nitrate with the methane or other carrier gas to be used. Rn^{220}(thoron) undergoes alpha decay with a half-life of 51.5 sec. to produce the alpha emitter, Po^{216}($t_{1/2}$=0.158 sec.). The Po^{216} alpha particles have a kinetic energy of 6.775 mev. (7) From considerations of conservation of momentum, the recoil energy of the Pb^{212} is calculated to be 0.128 mev. In helium under normal conditions of temperature and pressure, the Pb^{212} recoil range is calculated to be about 0.6 mm. (8)

The thoron-carrier gas mixture was allowed to stand in the reaction vessel at room temperature until the thoron was removed by decay, leaving Pb^{212}($t_{1/2}$=10.64 hr.) and its disintegration products as the only radioactive isotopes present. The carrier gas mixture had been previously dried after leaving the thorium nitrate solution by passage through a trap cooled with dry ice. After the thoron had decayed, the gases were expanded and condensed into a counter for determination of the gaseous activities present.

It was observed that volatile Pb^{212} compounds were formed in the presence of methane, propane, argon, and hydrogen, but not in the presence of helium. A 9:1 mixture of helium and methane produced only about 4% of the yield obtained for pure methane. The yield for pure hydrogen was very small, but detectable. On the other hand, the presence of argon seemed to enhance the yield of volatile lead. A 9:1 mixture of argon and methane produced about twice the yield obtained for pure methane. In addition, 100% argon produced nearly the same yield as obtained for the 90% argon-10% methane mixture.

The volatile products obtained with methane were trapped in a CCl_4 solution of $Pb(CH_3)_4$ at -13°C. and, when the solution was washed with aqueous lead nitrate, all of the Pb^{212} was extracted into the aqueous phase, indicating that $Pb(CH_3)_4$ was not a detectable product of the reaction.

It was observed also that about 50% of the CH_4 reaction products were immediately reactive with small amounts of oxygen, lowering the Pb^{212} content of the vapor. The volatile lead was condensable with liquid nitrogen and re-volatilizable under reduced pressure between -145° and -95°C. On standing at room temperature, the amount of volatile lead decreased slowly, being reduced to half in about 2 hours. Tests with the products obtained with pure argon seemed to show a similar instability with regard to retention in the vapor phase.

III. Reaction Mechanisms and Products

Although some of the characteristics of the recoil Pb^{212} products are known, the knowledge is insufficient to identify the compounds. The reaction mechanism, of course, cannot be elucidated until the reaction products are known.

A consideration of the ionization potentials of the various materials present has led to the conclusion that, since the ionization potential of lead is only about 7.5 ev., the lead probably reaches the end of its recoil path as a gaseous ion rather than as a neutral atom. It is reasonable to assume that equilibrium with respect to charge exchange has been obtained. The thermalized Pb^{212} can either react as an ion to produce volatile compounds or it can diffuse through the gas until it is neutralized by collision with the wall or by collision with a stray electron produced back along the recoil path.

After neutralization, the Pb^{212} could react with methyl radicals, for example, to produce volatile products. This could resemble the removal of lead mirrors with methyl radicals which has been shown to yield volatile $Pb(CH_3)_2$. (9) There has been reported evidence for the existence of dialkyllead compounds in solution, although they have not been successfully isolated. (10,11,12,13)

There is the further possibility that a hydride was formed in the recoil reaction, although the low yields with hydrogen would seem to indicate that PbH_4 is not a major product. The possibility of mixed alkyl hydrides would be good because of the increased stability expected to be obtained by substitution of alkyl groups for hydrogen in PbH_4.

Although the experimental evidence points strongly toward the production of some volatile lead-argon compounds, it is more probable in view of the chemical inertness of argon to have produced argon-sensitized reactions of the Pb^{212} with hydrocarbon or stopcock grease impurities present in trace amounts. This would be the expected situation with the mixture of 10% methane in argon.

IV. Conclusions

At the present time, it may be concluded that volatile lead compounds can be produced by recoil reactions in the gas phase and that relatively unstable compounds may be made available for study by these methods.

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ROLL CALL

MAGNETIC PROPERTIES OF SOME IRIDIUM COMPLEXES

Richard L. Carlin

The magnetic susceptibilities of several hexahaloiridate(IV) salts were measured by means of the Gouy and Sucksmith methods between room temperature and 77° K. (1) Contrary to expectation, magnetic moments that are smaller than those predicted for spin-only paramagnetism were observed. These data, together with the sign of the observed Weiss constants, indicate an antiferromagnetic interaction among the various iridium atoms. The metal-metal distance is consistent with this interpretation.

Similar results were previously reported (2).

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BINARY FLUORIDES

Stanley K. Madan

Dr. Peacock reported that when $W(CO)_6$ is led into liquid WF_6 a red solution is obtained, but no reduction occurs. Tungsten(VI) fluoride thus becomes an excellent solvent for unusual red-ox reactions. Using WF_6 as a solvent and $W(CO)_6$ as a reducing agent, he has been able to reduce ReF_6 and has isolated the products given in the following equation

$$W(CO)_6 + ReF_6 \xrightarrow{WF_6} ReF_5 + ReF_4 + ReOF_4.$$

The products undergo the following reactions

$$ReF_5 \underset{200^{o}C}{\rightleftarrows} ReF_6 + ReF_4$$

$$ReF_5 + H_2O \rightarrow ReF_6^{-2} + ReO_2 + ReO_4^{-2}$$

$$\underset{\text{blue}}{ReOF_4} \overset{\Delta}{\leftrightarrow} \underset{\text{black}}{ReOF_3}$$

$$ReOF_4 + H_2O \rightarrow ReO_2 + ReO_4^{-2}$$

Certain hexafluorides of group VIII elements can also be reduced, as

$$OsF_6 + W(CO)_6 \xrightarrow{WF_6} OsF_5 + OsF_4 + Os \text{ (metal -}$$

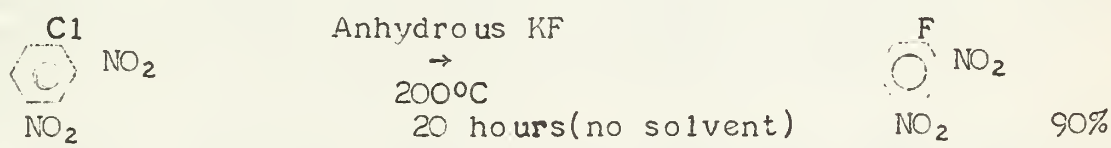
$$IrF_6 + W(CO)_6 \xrightarrow{WF_6} IrF_4 + IrF_3(?) \text{(no } IrF_5 \text{ could be found)}$$

R. D. Peacock, Technical Report ONRL-C-23-59 p.11

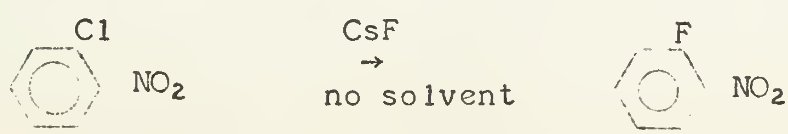
AROMATIC FLUORINE COMPOUNDS

Stanley K. Madan

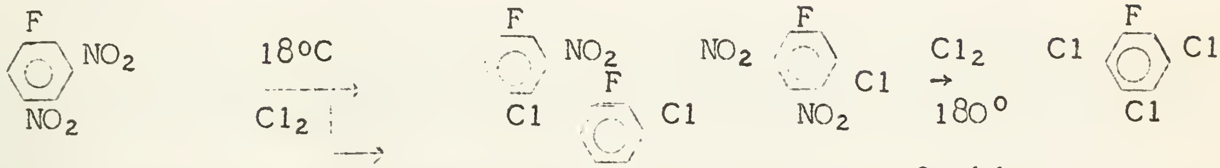
Prof. Vorozhotosov reported on the use of Group Ia fluorides for fluorinating substituted aromatic compounds at 200°C in absence of a solvent. For example chlorodinitro benzenes can be fluorinated as shown below:



Mononitro compounds, on the other hand, can only be fluorinated in the presence of CsF.



He also described some chlorination experiments on the dinitro compounds as shown by the reaction below



Another interesting reaction imvolved the nitration of chloro-fluoro benzenes and then reduction to give the amino compound.

N. N. Vorozhtosov, Technical Report ONRL-C-23-59 p. 6

REACTIONS OF PEROXYDISULFURYL DIFLUORIDE

N. J. Rose

Peroxydisulfuryl difluoride (PODD) has been prepared by Dudley and Cady (1) through the reaction between sulfur trioxide and fluorine in a silver difluoride catalytic reactor heated to 100°C. The PODD melts at -55.4°C and boils at 67.1°C. The structural formula

```
 O  O
OSOOSO
 F  F
```

is consistent with information obtained from vapor density molecular weight measurements, the infrared spectrum, the nuclear magnetic resonance spectrum, and hydrolysis studies.

Because the peroxy bond is probably the weakest bond in this molecule, Roberts and Cady (2) expected that SO_3F radicals might be present at high temperatures. Therefore, a reaction with sulfur dioxide was predicted which would yield a compound of empirical composition $S_3O_8F_2$. This reaction was tried by mixing streams of sulfur dioxide and PODD diluted with nitrogen in a nickel tube at 200°C. A compound isolated by vacuum distillation of the reaction products was tentatively assigned the following structure:

```
 O O O
FSOSOSF.
 O O O
```

Here again, the structure is consistent with information from vapor density molecular weight measurements, the infrared spectrum, the nuclear magnetic resonance spectrum, and hydrolysis studies. Either trisulfuryl fluoride or sulfuryl fluorosulfonate seems to be a correct name for the compound.

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SYNTHESIS AND RESOLUTION OF 1,2-PROPYLENEDIAMINETETRAACETIC ACID (PDTA).

R. E. Sievers

This preparation and resolution was undertaken in order to carry out ligand exchange studies with metal complexes in which the ligand is labeled by its optical activity.

Propylenediamine was condensed with chloracetic acid in alkaline solution at room temperature. After purification of PDTA, the Co(III) complex was prepared. Diastereoisomers were formed by introduction of the resolving agent d-cis-dinitrobis-(ethylenediamine)-cobalt(III) sulfate. Isolation of $[\underline{d}\text{-}\overline{Co}(en)_2(NO_2)_2\text{-}\underline{d}\text{-}Co(PDTA)] \cdot 2H_2O$ was effected by fractional crystallization. Recovery of the optically active acid was accomplished by decomposition of the cobalt complex. Cyanide and then copper(II) solutions were added to the cobalt complex with the resulting formation of $Cu(PDTA)^{2-}$. Extraneous cations were removed on an ion exchange column. The copper complex was decomposed with hydrogen sulfide and PDTA isolated by evaporation.

Reference

F. P. Dwyer and F. L. Garvan, J. Am. Chem. Soc., 81, 2955 (1959).

A POSSIBLE COMPLEX OF POTASSIUM WITH ETHYLENEDIAMINETETRAACETATE ION

Larry C. Thompson

The possible formation of a complex compound formed by the addition of potassium ions to Na_2H_2Y [Y = ethylenediaminetetraacetate (EDTA)] has been investigated by radiometric and potentiometric methods. The radiometric method was accomplished by measuring the activity of K^{42} in solutions containing Na_2H_2Y with $\mu = 0.1$ (NaCl), which had been equilibrated with either an anion or cation exchange resin, and comparing this with the initial activity.

The potentiometric method consisted of measuring the e.m.f. of a cell, one electrode of which was dependent upon $[K^+]$. The potential of the cell should change as [Y] was changed.

Both methods gave results that were independent of [Y], indication that there is no complexing of K^+ with EDTA.

Reference

B. P. Nikol'skii, A. M. Trofimov, and N. B. Vysokoostroskaya, Russian Journal of Inorganic Chemistry (English Translation), April, 1959, p. 389.

INNER COMPLEXES OF THE TYPE $Be_4O(RCOO)_6$

Catherine Travaglini October 20, 1959

I. INTRODUCTION

The reaction of Be^{++} with organic acids produces inner complexes of the type $Be_4O(O_2CR)_6$ (R = H or organic radical), which exhibit great stability. The tendency to form the "basic" derivative is so strong that normal salts form only with difficulty, the one exception being the formate (1).

The oxyacetate, first discussed in 1901, remains the best known and most thoroughly investigated, although the basic salts of many other organic acids have been reported. The list includes derivates of the acids crotonic; isocrotonic; levulinic; succinic; cyanoacetic; mono-, di-, and trichloroacetic; monobromoacetic; monochloro- and monobromopropionic; lactic; glycolic; ethyl- and phenylglycolic (or α-hydroxybutyric and mandelic, respectively); salicylic; benzoic (2); and 1- and 2-naphthoic (3).

The compounds formed are non-electrolytes and exhibit typically covalent properties: low m.p., and b.p., insolubility in water, solubility in organic solvents, and sublimation or distillation without decomposition. Their chemical properties include stability to heat, oxidation, and cold water; boiling water effects hydrolysis slowly. Mineral acids bring about decomposition to a berylliym salt, and the free acid.

The x-ray studies made in 1923 assign a unitary structure comparable with those ascribed to other strictly covalent compounds. A central oxygen atom is surrounded by four beryllium atoms linked by the acid groups bonded through the acid oxygen groups. Complete crystal symmetry occurs in the oxyformate and oxyacetate, but lower symmetry prevails in the higher acid analogs.

A review of the subject by K. N. Semenenko summarizes recent developments in the field (4).

II. METHODS OF PREPARATION

The methods listed below can, in general, be used for the higher acid analogs since they are similar to the acetate.

1. RCOOH + BeO or $Be(OH)_2$. (n-formate forms).
2. RCOOH + Basic Berylliym Carbonate
3. RCOOH or $(RCO)_2O$ + anhyd. $BeCl_2$. (n-formate forms).
4. RCOCl + Basic Berylliym compound. (Especially good for mixed basic derivatives.)
5. Miscellaneous: $Be(HCOO)_2 \rightarrow Be_4O(HCOO)_6$.

It is necessary to use non-reactive solvents such as toluene, xylene, benzene, chloroform, or carbon tetrachloride for extraction in order to prevent adduct formation.

The normal and basic formates and acetates are convertible under

the proper conditions:

$$Be_4O(CH_3COO)_6 + 2CH_3COOH + 2CH_3COCl \rightarrow 4Be(CH_3COO)_2 + (CH_3CO)_2O + 2HC$$

$$BeO + (CH_3CO)_2O \quad Be_4O(CH_3COO)_6 + (CH_3CO)$$

III. CHARACTERISTICS OF $Be_4O(CH_3COO)_6$

Basic berylliym acetate forms a stable cubic crystal with a diamond-like lattice, substituting in place of each carbon one whole oxyacetate molecule (5). The crystals, D = 1.39, m. p. 283°, and b. p. 330°, undergo several transformations to unstable forms.

Differential thermal analysis of a compound prepared from BeO and acetic acid revealed three transition points, 40°, 75°, and 125° (6), and a polymorphic transferance at 150°. The specific heat, measured between 24.4° and 58.8°, rose continuously up to 39.7° (150 cal./mole), then dropped suddenly within one degree to 125 cal./mole and remained nearly constant up to 54°. The transition at 40° is thought to be due to an order-disorder transition owing to the rotation of the carboxylic oxygens around the C-C bond (7).

A soft, wax-like phase, m.p. 285°, appears at 160°. This was reported to have a rhombohedral form and one molecule per unit cell (8). Recent work (9, 10) furnished information that the true structure is monoclinic with a=13.75kX, b=9.24kX, c=16.21kX, and α=98°55', with four molecules per unit cell. This transforms on standing into the more stable cubic modification. Comparable results are obtained from the oxyacetate precipitated from hot butanol or hot tetralin, crystallized from the melt, or sublimed (11). The relationship of the modification is found to be:

CUBIC MODIFICATION $\xrightarrow[\text{Slow Cooling}]{148^\circ}$ HIGH-T-MODIFICATION

Depends on transformation time — MONOCLINIC β — quick cooling

IV. PROPERTIES OF OTHER ORGANIC ACID DERIVATIVES

Berylliym oxyformate is produced indirectly only by the double decomposition of basic salts with anhydrous formic acid, followed by heating the normal salt above 250° (12). Orthorhombic prisms form,

$$Be_4O(CH_3COO)_6 + 8HCOOH \rightarrow 4\ Be(HCOO)_2 + 6CH_3COOH + H_2O$$

$$BeO + H_2O + 2CO \qquad Be_4O(HCOO)_6 + H_2O + 2CO$$

with cell dimensions of 14.4, 11.7, and 7.4kX (14).

As the acid radical becomes more complicated, two separate salts, a normal and a basic one, as for the formate and acetate, no longer form, but instead mixed crystals result (15). Small, birefringent prisms of the basic monochloroacetate (m.p. 181°) form, but are of variable composition between that of the normal and oxy salt, but crystallized in the lattice form of the oxy compound. Similar results are obtained from the basic monobromoacetate and propionate, which form monoclinic

crystals that decompose above 95° to the true oxysalt with no crystal structure change.

A phase diagram of the system $Be_4O(CH_2ClCOO)_6$-$Be_4O(CH_3COO)_6$ shows two compounds of intermediate composition, but demonstrated to be individual by x-rays (16). The derivatives are $Be_4O(CH_3COO)_4(CH_2ClCOO)_2$ and $Be_4O(CH_3COO)_2(ClCH_2COO)_4$, and exhibit triclinic lattices.

The oxybenzoate, formed from the basic carbonate added to the fused acid, has a low temperature monoclinic modification, m.p. 317°, with elementary crystal parameters of a=21.02, b=12.28, c=34.05kX, $\beta=91^{\circ}$ (2,18).

1- or 2-Naphthoic acid reacts with freshly prepared $Be(OH)_2$ to yield the 1-salt, m.p. 246.5°, or the 2-salt, m.p. 335.5-336.5° (3).

V. INCLUSION COMPOUNDS OF BASIC SALTS

A variety of addition compounds form with many organic solvents, especially the alcohols and amines. The ethanol adduct of the oxyacetate has an x-ray pattern resembling that of the simple oxyacetate (20). Pure basic salt sublimes at 200° after loss of ethanol and acetic anhydride. Evidence of a polymeric higher basic acetate exists, $Be_4O_m(CH_3COO)_{8-2m}$.

Heating the oxyacetate with methanol or butanol produces Be(OR)OCOCH$_3$, which on hydrolysis yields the alcohol (21), as well as a product similar to the above polymer, e.g., $3Be(OH)O_2CCH_3 \cdot Be(C_4H_9O_2)CH_3COO$, probably with the structure ...Be-O-C=O...Be-O-C/O...

The alcohol content of the methanol adducts of the higher basic acetates exceeds that of the analogous ethanol products (22). The gels have liquid x-ray patterns, but do not liquefy on warming. After one to two years, a stable branched chain or layer structure of $[Be_4O_m(CH_3COO)_{8-2m}]_n$ (m 1, n=2.4), containing the monoclinic α-form of the monomeric acetate, forms.

Solvent-adducts of the higher alcohols, polymers formed by loss of acetic anhydride, contain both α and β forms of the oxyacetate (23). In general, the higher the molecular weight of the alcohol, the less adduct formation.

Pyridine-adducts are shown by their decomposition polytherms to have pyridine dissolved in the crystal lattice of the basic salt (25). The first two pyridine molecules of the adduct, $Be_4O(CH_3COO)_6 \cdot 3C_5H_5N$, are loosely bound, but removal of the third pyridine causes decomposition:

$$Be_4O(CH_3COO)_6 \cdot 3py \rightarrow Be_4O(CH_3COO)_6 \cdot 2BeO \ (26).$$

The crystalline product containe one to three moles of pyridine per mole of acetate, but the amorphous product contains less than one mole of pyridine per mole of acetate.

Dioxane adducts of the basic acetate, propionate, and formate are converted to their simple salts on long stirring in chloroform or acetone but stirring with pyridine produces the pyridine-adduct of the acetate. The dioxane inclusion compounds decompose in water and lose dioxane in air.

Dry ammonia forms a series of compounds with the acetate (27):

$$Be_4O(CH_3COO)_6 \xrightarrow[CHCl_3]{NH_3} Be_4O(CH_3COO)_6 \cdot 2NH_3 \xrightarrow[CHCl_3]{NH_3} Be_4O(CH_3COO)_6 \cdot 3NH_3$$

III, IV

A white, hygroscopic powder, $Be_4O(CH_3COO)_6 \cdot 2NH_3$, has also been reported. It is unstable in water, ethanol, and chloroform (28). Unstable inclusion compounds of the basic acetate with methyl- and ethylamine and sulfur dioxide have also been produced. Reaction of the basic compound with NH_4HF_2 results in BeF_2 (29).

Higher-basic salts such as $Be_4O_m(O_2CEt)_{6-2m}$ (1 m 4) form similar inclusion compounds (30). The oxybenzoate-solvent adducts consist of a molecule of ligand included in the hollows of the crystal lattice; the interaction between components is small (18).

It was hoped that polymeric basic beryllium carboxylates with the basic structure in both the polymer chain and as a substituent in the polyethylene chain would maintain the high thermal stability of the monomer (31). The linear condensation polymer was formed by replacing two of the monobasic carboxylic groups by carboxyl groups of dibasic acids,

$$nBe_4O(CH_3COO)_6 + nXOCR'COX \rightarrow \left[\left(\begin{matrix} Be_4O \\ (RCO_2)_4 \end{matrix} \right) \begin{matrix} O \\ \\ O \end{matrix} CR'C \begin{matrix} O \\ \\ O \end{matrix} \right]_n + 2nRCOX.$$

The desired thermostability was not found, as the product disproportionates to form the monomer and a cross-linked polymer, $-[Be_4O(O_2C-R'CO_2)_3]_n-$, even at room temperature.

VI. CONCLUSION

The entire properties of the basic oxy-salts furnish a new example of the always peculiar behavior, because of size, of the first element in each column. Further examination of the possibility of forming stable and useful polymers seems warranted.

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HALOGEN FLUORIDES AND SOME OTHER COVALENT FLUORIDES

Edward J. Friihauf October 27, 1959

I. Introduction

Since World War II, interest in fluorine-containing compounds has increased tremendously. The halogen fluorides and other similarly covalent fluorides are active fluorinating agents and, as such, have received much attention. The knowledge of the chemical and physical properties of these fluorides is far from complete and more thorough investigation is certain to follow. The chemistry of these covalent fluorides has been reviewed by several authors. (1-4)

II. Preparations and Chemical Properties

A. Halogen Fluorides

ClF, ClF_3, BrF, BrF_3, BrF_5, IF, IF_3, IF_5, IF_7

All of the halogen fluorides can be obtained by direct combination of the elements. However, in some cases more nearly pure products are obtained by other methods. (3) Iodine monofluoride and iodine trifluoride have not yet been isolated.

All of the halogen fluorides act as active fluorinating agents although much of the information available is qualitative. Under the proper conditions, the halogen fluorides appear to react with all organic materials; with all of the metals; all of the nonmetals with the exception of oxygen, nitrogen, and the inert gases; and with salts to form the corresponding fluorides. The approximate order of reactivity is $ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$.

B. Group V Fluorides AsF_5, SbF_5, VF_5, NbF_5, TaF_5

Each of the above fluorides can be obtained by direct fluorination at 300-500°C. Bismuth pentafluoride is saltlike.

Information concerning the chemical activity of these covalent fluorides is less complete than for the halogen fluorides. Owing to the stability of the lower valence states of the elements of Group V, the pentafluorides are expected to be active fluorinating agents.

C. Group VI Fluorides

SF_6, SeF_6, TeF_6, SF_4, SeF_4, TeF_4, MoF_6, WF_6, UF_6

Sulfur, selenium, and tellurium hexafluorides can be prepared directly from the elements, whereas the other hexa- and tetrafluorides require different methods. (3)

All of the hexafluorides can behave as fluorinating agents under the proper conditions. Considering the other fluorides already reviewed, very little has been reported about the chemistry of the tetrafluorides. Recently, sulfur tetrafluoride has been reported to replace oxygen with fluorine in organic compounds, (5) and to yield the

following covalent fluorides in high yields from the corresponding oxides: IF_5, SeF_4, MoF_6, UF_6, WF_6. (6)

III. Physical Evidence for Association and Ionization

A. Halogen Fluorides

Few physical data are available for bromine monofluoride because of its instability. All the other halogen fluorides seem to be associated in the liquid state, as evidenced by the large values calculated for Trouton's Constant. Specific conductivity measurements suggest that bromine trifluoride, iodine pentafluoride, and bromine pentafluoride exhibit some degree of self-ionization. Nuclear magnetic resonance studies suggest that chlorine trifluoride and iodine pentafluoride are associated in the liquid state. (7) The structures of the halogen fluorides are known with the exception of iodine heptafluoride, where data are incomplete. Bromine and chlorine trifluorides have a distorted planar T structure, and bromine and iodine pentafluorides may be pictured as a tetragonal pyramid with a lone electron pair in the sixth octahedral position.

B. Group V Fluorides

High boiling points and high Trouton's Constants suggest that all of these covalent pentafluorides are associated in the liquid state. The specific conductivity values for vanadium, niobium, and tantalum fluorides suggest partial self-ionization. (8) Nuclear magnetic resonance studies of antimony pentafluoride give evidence for association in the liquid state. (9) The structures of most of these fluorides are unknown. The most probable structures are a trigonal bipyramid, as in PF_5, or a tetragonal pyramid, by analogy with IF_5.

C. Group VI Fluorides

Low boiling points or sublimation points and normal Trouton's Constants suggest that the hexafluorides are not associated in the liquid state. There seems to be very little evidence for self-ionization. The hexafluorides have the octahedral structure.

In contrast, all of the tetrafluorides seem to be associated in the liquid state, as evidenced by nuclear magnetic resonance studies. (10) The structure of the tetrafluorides may be visualized by placing five pairs of valence electrons in trigonal bipyramidly directed sp^3d hybrid orbitals with the unshared pair in an equatorial orbital. (11)

IV. Chemical Evidence for Association and Ionization

A. Halogen Fluorides

The only two halogen fluorides reported to show chemical evidence for ionization are bromine trifluoride and iodine pentafluoride. If a solvent MF_n ionizes according to the equilibrium

$$2MF_n \rightleftarrows MF_{n-1}^+ + MF_{n-1}^- ,$$

then soluble compounds yielding the MF^{+}_{n-1} ion are called acids and soluble compounds yielding the MF^{-}_{n+1} ion are called bases. In the iodine pentafluoride system, the acid $IF_4^{+} \cdot SbF_6^{-}$, the base $K^{+} \cdot IF_6^{-}$, and the solvolyzed salt $KSbF_6 \cdot 0.23IF_5$ have been isolated and described. (12) In the bromine trifluoride system, many acids, bases, and salts have been isolated, and together with good conductometric titration curves, this evidence suggests that bromine trifluoride is the parent for another solvent system.

B. Group V Fluorides

The pentafluorides of Group V elements all appear to form the MF_6^{-} ion in bromine trifluoride solution, and salts containing this ion have been isolated. (4) This may lead one to suspect that these pentafluorides display self-ionization.

C. Group VI Fluorides

Preliminary evidence for the self-ionization of selenium tetrafluoride has been reported. (13, 14) There is little chemical evidence for the other Group VI fluorides.

V. Fluorine as a Bridge Former

Perhaps the best known case of fluorine participating in bridge formation is liquid HF. However, this is generally cited as an example of hydrogen bonding. The compounds Tl_2AlF_5 (15) and $CsSb_2F_7$ (16) have bridging fluorine atoms as shown by X-Ray measurements. The 1:1 addition compounds of boron trifluoride with triethyl amine and pyridine can absorb a second equivalent of boron fluoride to form relatively unstable 1:2 addition compounds. These 1:2 adducts probably have a bridging fluorine atom. (17) More recently, nuclear magnetic resonance studies of the compounds $2AsF_3 \cdot 3SO_3$ (18), SbF_5 (9), and $SbF_5 \cdot AsF_3$ (19) give evidence for fluorine bridging. The nuclear magnetic resonance studies of ClF_3, BrF_3, and IF_5 suggest that the observed fluorine exchange goes by means of an association mechanism involving fluorine bridges. (7) Also bridge formation is said to account for the observed rapid fluorine exchange in SF_4(10) and for the molecular structure of the compound $SbF_5 \cdot SF_4$ (6).

Fluorine exchange does not always proceed through fluorine bridged dimers. Rapid fluorine exchange has been observed between labeled HF and other covalent fluorides in both the liquid and vapor states. (21) The vapor state exchange reaction between HF and ClF_3 is postulated to occur through formation of a covalent intermediate $HClF_4$. Evidence for this covalent intermediate is from spectral studies. (22)

VI. Summary

The most recent investigations have shown the importance of fluorine-bridged dimers and association complexes in the chemistry of the covalent fluorides. Further investigation may show that some of these covalent fluorides are possibly the parents of new solvent systems.

TABLE I

PHYSICAL CONSTANTS OF THE HALOGEN FLUORIDES AND

SOME OTHER COVALENT FLUORIDES

	F.P., °C.	B.P., °C.	Trouton's Constant	Specific Conductivity, ohm^{-1} cm^{-1} at 25°C.
ClF	-154	-100	28	--
ClF_3	- 83	11.3	23.1	3.9×10^{-9}
BrF	- 33	- 20	20.5	--
BrF_3	8.8	127.6	25.7	8.0×10^{-3}
BrF_5	-61.3	40.5	23.2	9.1×10^{-8}
IF_5	9.6	98	26.3	5.4×10^{-6}
IF_7	5-6	4.5 subl.	--	--
VF_5	20	48	33.1	2.4×10^{-4}
NbF_5	80	235	25.4	1.63×10^{-5} at 80°C.
TaF_5	95	229	25.9	1.56×10^{-5} at 95°C.
AsF_5	- 80	- 53	23.6	--
SbF_5	9	143	25.9	1.2×10^{-8}
SF_6	- 50 press.	-63.5 subl.	--	--
SeF_6	- 34.7 press.	-45.9 subl.	--	--
TeF_6	- 37.7 press.	-38.4 subl.	--	--
MoF_6	18	35°	21	--
WF_6	2	17°	21.5	--
UF_6	69.2 press.	56.2	--	--
SF_4	-121	- 40	27.1	--
SeF_4	- 9	106	30.0	--
TeF_4	129	--	--	--

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CHEMICAL INTERACTIONS AMONG DEFECTS IN GERMANIUM AND SILICON

Ricardo Ferrus November 3, 1959

I. INTRODUCTION

The preparation of large pure single crystals of silicon and germanium in recent years has permitted one to study chemical reactions in both elements (1), considered as new reaction media.

Investigations in these particular media have been stimulated by the analogy between semiconductors and aqueous solutions.

II. DEFECTS AS SOLUTES

The chemical entities in reactions which take place in silicon or germanium crystals are the defects or imperfections in the crystal lattice. Important imperfections from a chemical point of view are (2) conduction electrons and holes, interstitial atoms, lattice substitutions, and vacant lattice sites. The last are important in non-stoichiometric compounds and need not be considered here.

In a semiconductor, there are two important kinds of electrons, conduction electrons and valence electrons separated by the forbidden energy gap characteristic of the semiconductor. One electron missing in the valence band is considered as a hole, p, with charge e^+. (3)

The second kind of imperfection to be considered is that due to intertitial atoms, which give off electrons and remain as interstitial cations in the lattice. In our case, the only studied defect of this kind has been that produced by lithium. No interstitial acceptor atom is known.

Finally, we have substitutional defects. We are concerned with the diamond-type lattices of group IV elements. Atoms from group III and group V elements are able to enter this lattice in a substitutional way, acting as electron acceptors or donors, respectively.

III. FERMI LEVEL

Electrons in a Fermi-Dirac system follow the distribution law

$$f(E) = \frac{1}{1 + \exp \frac{E-E_F}{kT}}$$

where E_F is a parameter, "Fermi level", that it is shown to be equal to the electrochemical potential, or partial molal free energy per electron.

IV. SIMILARITIES BETWEEN SEMICONDUCTOR AND AQUEOUS SOLUTIONS (4)

Holes in semiconductors play an identical roll to hydrogen ions in water, and electrons are the counterpart of hydroxide ion. The portion of the Fermi level in the forbidden gap becomes analogous to the pH of an aqueous solution. Semiconductors with more conduction electrons

than holes (n-type) are "basic", and the Fermi level is in the upper part of the forbidden gap. Conversely, if the number of holes is higher, we have "acidic" semiconductors (p-type), and the Fermi level is in the lower part.

Donor impurities then act as bases and acceptors as acids. The process of titrating or neutralizing an acid by a base is analogous to that of compensating an acceptor with a donor. It is possible to reproduce the "buffer" effect in semiconductors using weakly ionized donor and acceptor elements or amphoteric elements.

V. SOLUBILITY EQUILIBRIA

A. Effect of Hole-Electron Equilibrium

For a solute D which is in equilibrium both with a semiconductor, (D^s), and an external, (D^e), phase in which its activity is constant, the following equilibria may be written

$$D^e \underset{}{\overset{K_1}{\rightleftharpoons}} D^s \underset{}{\overset{K_2}{\rightleftharpoons}} D^+ + e^-$$

Any variation in the concentration of e^- will, through the mass-action effects, change the ionization and therefore the solubility of D. Theoretical predictions (5) have been confirmed experimentally. (6)

B. Effect of Ion-Pairing on Solubility

An effect on the solubility from the pairing of ions of opposite signs is to be expected. The magnitude of such an effect has been calculated (7) by taking account of the fact that the equilibrium to form pairs, P

$$A^- + D^+ \rightleftharpoons P$$

may be expressed in terms of an ion-pairing constant Ω_p

$$\frac{N_P}{N_{A^-} N_{D^+}} = \Omega_p$$

where N_P, N_{A^-}, and N_{D^+} are the concentrations of pairs and free ions in the semiconductor. Experimental results (6) show a fair agreement with calculations.

VI. ION-PAIR PHENOMENA

The central feature of the Debye-Hückel theory is the concept of the ionic atmosphere. When the dielectric constant of the medium decreases and the total ionic concentration increases, a stage is reached in which the atmoshperes of some of the ions may be best thought of as being fully constituted by a single ion of opposite sign, so that an ion pair forms. This situation is particularly favored in solid solvents, where there is no solvation to deal with and where ion-pair formation should be more pronounced than in aqueous solutions, both because of the lower dielectric constants and the closer approach of the ions in the solids.

A. Ion-Pairing Relaxation

At sufficiently high temperatures, the pairs are completely dissociated, and the ions are randomly distributed. If the temperature is suddenly decreased to a value where pairs form, a reaction ensues to which a rate constant, k, may be assigned. (6)

B. Interaction of Ion Pairs with Carriers.

Impurities in semiconductor crystals introduce energy levels in the forbidden gap. When an ion pair forms, there is a removing of states from the forbidden gap which were available before the pairing; the effect arises from the coulombic repulsion by the dipole on the hole and electron liberated by the ionized acceptor and donor, respectively. Theoretical prediction nearly fits experimental results. (8)

C. Ion Triplets

If one of the pairing ions is a doubly charged ion like $Zn^{=}$, possibility of triplet formation appears. (6) Morin and Reiss (9) have made a quantitative study of the triplet $(Li^{+})_2Zn^{=}$ in germanium.

VII. COMPOUND FORMATION IN SEMICONDUCTORS

Following the analogies between aqueous solutions and semiconductors, the formation of ionic, metallic, or covalent bonds between solute particles has been suggested. (6)

Electrical investigations on silicon crystals show the presence of oxygen compounds formed with other solutes such as Al, B, Ga, and possibly In. (10)

Pell (11) has reported the interaction between Li and oxygen and has been able to calculate the equilibrium constant for reaction

$$Li^{+} + O \rightleftharpoons LiO^{+}$$

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MECHANISMS FOR ELECTRON TRANSFER REACTIONS

L. J. Sacks November 10, 1959

I. Introduction

Since all chemical reactions involve electron transfer to some degree, the first requirement for an analysis of possible mechanisms is a restriction of the topic. Therefore, only redox systems are treated here. Our present knowledge is sufficiently limited that the possibility of useful discussion of more than the simplest cases is questionable. However, even in the simplest case, the exchange between different oxidation states of the same metal, the processes are sufficiently complicated and the information gained sufficiently valuable to warrant careful consideration.

Because of the physical measurements generally required,* most investigations have been relatively recent, and theoretical advances are still in the formative stages. A recent review by Taube (2) indicates the complexity of the problem. Even for such "simple" systems as Fe(II)-Fe(III), exchange may proceed by a variety of paths. Hexacyanoferrate(II,III) exchange proceeds very rapidly (3), yet the aquated $Fe^{+2,3}$ ions exchange but slowly (4); on the other hand, $Co^{+2,3}$(aq), although very similar in size and charge to the corresponding iron ions, exchange extremely rapidly (5), whereas the cobalt hexammines exchange very slowly (6).

In this presentation the primary factors governing electron exchange are reviewed, and examples illustrating these factors are given. Suggested mechanisms are critically reviewed.

II. Requirements for Electron Exchange

A. Energy Considerations.

According to the Franck-Condon principle (7), transfer of an electron is sufficiently rapid that no nuclear vibrations can occur in either the electron donor or acceptor during this transfer. This requires that the energies of the exchanging partners be matched <u>before</u> electron transfer can occur (8,9). Such matching constitutes the prime energy requirement for transfer. Several energy terms must be considered.

In redox reactions involving transition-metal ions, an important consideration is the crystal field stabilization (CFS) energy of each oxidation state. Where large changes occur, as in the case of cobalt complexes with EDTA (10), such differences may account for the low observed rates. The similarity of exchange rate between between Fe^{+2} and FeX^{+2} ($X = Cl^-$, Br^-, OH^-, F^-) led Adamson and Vorres to the conclusion that "this common rate controlling factor is the nature of the

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* A notable exception is the work of Dwyer and Gyarfas (1). Using optically active oxidant and reductant with ligands of opposing rotatory orientation, they were able to follow the electron transfer by the change in rotation.

crystal field energy levels for the two species" (11).

Associated with every ion in solution is a surrounding shell of solvent molecules. Hydration energies are particularly large, ranging as high as 10^3 kcal for Al^{+3} (2), and changes in oxidation state undoubtedly are accompanied by substantial changes in aquation, necessitating considerable rearrangement.

In addition to energies associated with the Franck-Condon requirements, there arises the problem of transporting the electron across the space from the reductant to oxidant. Two approaches may be taken. In the first, the ligands and solvent, both bound and free, may be treated as an energy barrier and the transfer of the electron considered in terms of quantum mechanical barrier-tunnelling (12). Since probabilities are involved, the interpretation may be made in terms of activation entropy. Marcus (9) has estimated rates on this basis, but since his calculations assumed small, constant differences in energy of the partners, predictions do not hold where varying CFS energies are involved.

B. Closeness of Approach.

Gas-phase studies of electron exchange between rare-gas ions and their parent atoms (13) give a collision cross-section of several Bohr radii. For complex molecules, considerably greater effective radii are found, reflecting the greater ease of energy-matching through vibrational contributions. The large distances suggest that a quantum mechanical calculation of exchange probability _vs_. internuclear distance would give useful information. Since shielding by other electrons for a test electron at considerable distance from the nucleus is essentially complete, the hydrogen molecule-ion offers a good approximation as a working model (8). Electron transfer predictions may then be derived from the exchange integral. Libby (8) has shown that for the _3d_ orbital, interactions at appreciable distances occur with considerable frequency. Along the internuclear axis, the exchange frequency for H_2^+ at equilibrium distance, r_o, is ca. 7×10^{15} sec^{-1}. At 5 Å the value is ca. 7×10^{13}; at 15 Å, ca. 10^{11}; and at 20 Å, ca. 2×10^8. Of course, no energy barrier to electron transfer has been considered.

C. Coulombic Forces.

High probabilities for exchange even at great distances allow an explanation for rapid exchange between ions displaying strong coulombic repulsions. The very rapid exchange of the hexacyanoferrate(II and III) ions may be considered evidence for long-range exchange. An alternate mechanism has been suggested by Zwolinski (14). Consider the approach of aquated Fe^{+2} and Fe^{+3} ions. At a distance of 2 Å, coulombic repulsion between the ions, neglecting the dielectric constant of the medium, would be about 10^3 kcal. If, however, a chloride ion were located between the two ions at a distance of 2 Å from each, a net attraction of 300 kcal. $mole^{-1}$ would result. According to Gates and King (15), however, such "outer sphere" interactions - beyond the first coordination sphere of the ion - are quite small.

III. Specific Mechanisms.

A. Bridged Activated Complexes.

The most detailed, careful work in the field of mechanisms has been done by Taube and his co-workers (2, and references listed therein; 16, 17). A typical system is the exchange between $[(NH_3)_5Co\overset{*}{C}l]^{+2}$ and $Cr^{+2}(aq)$. Using radioactive chlorine (Cl^*), they found that Co(III) does not exchange chloride ion with the solution, but that Cr^{+2} complexes with either chloride ion or water in the coordination sphere are highly labile. In the case cited, it was found that Cr(III) appeared exclusively as $Cr\overset{*}{C}l^{++}$, and that this species does not exchange Cl^- with the solution to an appreciable extent in the time required for measurements (18). Such appearance of the radioactive chlorine in the chromic species can only be interpreted as evidence for a $[Co-Cl-Cr]^{+4}$ species in the transition state. In addition to chloro-bridges, other anions have varying degrees of effectiveness in promoting electron transfer. In general, ions which bring the redox partners to favorable distances (F^-, Cl^-, OH^-) or those which allow free electron passage (e.g., conjugated anions of organic acids) give higher rates of exchange. The high rates with such anions as sulfate, phosphate, or pyrophosphate are less easily explained, although multiple bridging has been suggested (2). The exchange between the aquopentammine-cobalt(III) ion and chromous ion indicates parallel processes, one due to OH^- formed by ionization of the coordinated water molecule, the other to H_2O transfer.

In order to interpret rates for reactions in which bridging groups are involved, it is necessary to consider not only the bridging ability of the group, but also the distance at which electron transmission probability is the greatest; crystal field and hydration energies (for energy matching); and variation in the potential barrier between the partners with ligand structure. Only the most qualitative attempts have thus far been made (2). It is not clear whether bridge formation occurs only at the time of electron transfer or whether a meta-stable intermediate is first formed. Taube suggests the possibility of the latter for systems he has studied (2). A system in which such poly-nuclear species are likely is the Ce(III)-Ce(IV) couple. Bi-nuclear $[Ce-O-Ce]^{+6}$ has been proposed by Fronaeus and Ostman (21) to explain the observed exchange rates. Conclusive evidence for a Ce(III)-O-Ce(IV has, unfortunately, not been found.

B. Exchange in Which No Bridging Is Involved.

In complexes such as hexacyanoferrate(II or III) or hexammine-cobalt(II or III), transfer does not occur through bridging groups (at least not of the first coordination sphere of the metals). The observe rates are readily explicable in terms of crystal field energies if one allows transmission over considerable distances. Hexacyanoferrate-(II and III) ions are examples of strong octahedral fields, hence the ferrous and ferric ions will have, respectively, six and five electrons in d_ϵ . Thus, redox would not be expected to be accompanied by appreciable changes in the ligand field orientation, energy matching should be relatively simple, and rapid rate of exchange would be

expected. Other than an approximate (and very high) reported rate (3), this rate is generally considered to be immeasurably fast. Similarly, manganate and permanganate ($\underline{d}^1$ and $\underline{d}^0$) should be expected to exchange rapidly, as is found (19). Tracer studies with labeled oxygen show no exchange by either of these ions with water. Arguments in terms of symmetry properties merely reflect these factors, and suggestions that there is some fundamental advantage to "symmetrization" (20) serve more to becloud the issue than clarify it.

The EDTA complexes of cobalt provide an interesting example of transition from weak (Co(II)) to strong field (Co(III)). With two electrons in d_{γ}, it would be expected that ligands along the Z-axis in Co(II) would have an equilibrium distance greater than for a ligand on the Z-axis of Co(III), which has no $\underline{d}_{\gamma}$ electrons. The slowness of this exchange (11) emphasizes the importance of energy matching. Surprisingly, the authors (11) interpret this slowness in terms of changes in electron pairing *per se*.

IV. Conclusions.

No single factor can determine the rate of electron change. The primary requirement of energy matching must be met if a rapid process is to ensue. This can often be met in strong crystal fields of the ions, provided both oxidized and reduced forms are of comparable field strength and configuration. If energy matching is readily possible, secondary factors probably determine the exact rate: coulombic forces and counter-ion nature, bridging possibilities and, perhaps, factors as yet to be discovered. Whether bridging groups allow better energy matching as well as providing an electron path has not been established.

More carefully obtained experimental data are needed. Many reported rates are unreliable, owing to apparent impurities or difficulties in separation procedures. It is hoped that with an expanding body of data--particularly, as suggested by Taube (2), in non-aqueous media--more quantitative estimates of the various factors will be possible and application to the multitude of waiting problems will be feasible.

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RECENT ADVANCES IN THE CHEMISTRY OF METAL-AROMATIC COMPOUNDS

R. E. Eibeck November 17, 1959

I. INTRODUCTION

Since the discovery of ferrocene in 1951, investigation of such metal-aromatic compounds has increased very rapidly, with over two hundred publications appearing by the end of 1957. The most prolific investigator in the field has been Dr. Emil Otto Fischer of the University of Munich. His name appears on approximately fifty publications in this six-year period. Recently Dr. Fischer and Dr. H. P. Fritz have compiled an excellent review entitled "COMPOUNDS OF AROMATIC RING SYSTEMS AND METALS."[44]

The following discussion is intended to be a review of the pertinent publications which have appeared in 1958 and 1959.

As a basis for further discussion, metal-aromatic compounds shall be defined as those compounds, such as ferrocene $Fe(C_5H_5)_2$, in which a metal atom is bonded to a cyclic organic molecule by an even number (usually six) of easily polarizable π- electrons.

For the purpose of brevity the following abbreviations are used in the text:

Cp = $C_5H_5^-$

CpH = C_5H_6

Ar = Benzene or benzene derivative

CHT = $C_7H_7^+$

Me = Metal

II. A NEW SYNTHETIC METHOD

In 1958, three publications describing a new method for the synthesis of aromatic metal-carbonyl compounds appeared. This situation is an interesting case of simultaneous discovery, since the three reports were published in three different countries: Nicholls[36] in England, Fischer[14] in Germany, and Natta[35] in Italy.

It was observed that when an aromatic hydrocarbon was heated under pressure with a metal carbonyl, such as $Cr(CO)_6$, carbon monoxide was given off, and an aromatic-metal carbonyl compound was formed. The reaction conforms to the following stoichiometry.[14]

$$Me_x(CO)_y + zAr \rightarrow Me_x(CO)_{y-3z}Ar_z + 3_z CO.$$

This new synthetic method has been applied mainly to the elements of periodic family VI B (Cr, Mo, W) and leads to a large number of new diamagnetic, sublimable complex compounds of the type $ArMe(CO)_3$.

III. SPECIFIC COMPOUNDS

A. Family IV B

Compounds of the type $CpTiX_3$ and Cp_2TiX_2 have been synthesized by the following reactions:[40]

$$Mg(Cp)_2 + 2TiX_4 \rightarrow MgX_2 + 2CpTiX_3$$

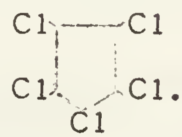
and $$Mg(Cp)_2 + TiX_4 \rightarrow MgX_2 + Cp_2TiX_2$$

where X = Cl, Br, I.

Physical evidence suggests that the Cp ring in $CpTiX_3$ is bonded as in ferrocene thus producing what might be called an "open sandwich" structure.

$CpTiCl_3$ may also be formed in other ways as follows:[25]

$$Cp_2TiCl_2 + TiCl_4 \xrightarrow[\text{24 hrs. p-xylene}]{120^{\circ}} CpTiCl_3 \quad (85\%)$$

or $$Cp_2TiCl_2 + Cl_2 \xrightarrow[60^{\circ}]{CCl_4} CpTiCl_3 +$$ 

One other compound has been obtained as follows:[34]

$$Cp_2TiCl_2 + 2NaCp \rightarrow \text{intermediate} \xrightarrow[\text{135 atm. } 100^{\circ}C \text{ 8 hrs.}]{CO} Cp_2Ti(CO)_2$$

$$Cp_2TiCl_2 + 2LiBu \rightarrow (?) + CO \rightarrow Cp_2Ti(CO)_2$$

B. Family VB

The compound $CpV(CO)_4$ reacts with HCl and O_2 to form the compound $CpVOCl_2$,[20] a sublimable, diamagnetic, blue-black solid. Cyclopentadienyl vanadium tetracarbonyl may also be reduced with sodium in liquid ammonia to yield the ionic compound $Na_2[CpV(CO)_3]$,[21] which probably contains vanadium in the -1 oxidation state. The $[CpV(CO)_3]^{-}$ ion is isoelectronic with $Cp\,Mn(CO)_3$ and $CpCr(CO)_3^{-}$.

Very recently, King and Stone[30] have reported the synthesis of the compound $C_7H_7^{+}VoC_5H_5^{-}$ by the following method:

$$CpV(CO)_4 + C_7H_8 \xrightarrow[N_2 \; 120^{\circ} \; \text{9 hrs.}]{\text{reflux}} \text{low yield } CpVCHT.$$

The substance was obtained as purple crystals, and magnetic measurements show one unpaired electron, thus suggesting a vanadium(O) compound.

It has been suggested[32] in a publication on the Proton Magnetic Resonance spectrum of Cp_2V that this compound may be oxidized to $VOCp_2$.

C. Family VI B

1. Chromium - E.O. Fischer and coworkers have reported the syntheses of $(C_4H_4S)\ Cr\ (CO)_3$[15] and $C_5H_5CrC_6H_5$[13]. The latter compound was obtained by allowing $CrCl_3$ to react with a 1:1 mixture of ØMgBr and CpMgBr.

The reaction of ØMgBr with the chromium halides in Et_2O, followed by hydrolysis under N_2, leads to a mixture of $(C_6H_6)_2\ Cr$ and $(C_6H_6)(C_{12}H_{10})Cr$.[43] These π- complexed products are considered to be formed by an internal rearrangement of σ-bonded phenylchromium intermediates.

Reference has already been made to the work of Nicholls[36] in synthesizing compounds of the type $A_RCr(CO)_3$. A similar publication has been presented by Fischer[8].

By allowing $M(CO)_6$ to react with the methiodides of pyridine, quinoline, and acridine, Moore and Wilkinson have obtained a series of heterocyclic sandwich compounds.[33]

2. Molybdenum - If azulene, $C_{10}H_8$, is refluxed with $Mo(CO)_6$ in petroleum ether, one obtains $C_{10}H_8Mo_2(CO)_6$[3] as black, paramagnetic crystals.

Other molybdenum compounds reported are as follows: $C_7H_8Mo(CH)_3$ [1], $(C_7H_8)_2\ Mo_2(CO)_6$,[1] $C_8H_{10}Mo(CO)_3$,[17] and $(C_8H_{10})_2\ Mo(CO)_2$.[17] From $C_7H_8Mo(CO)_3$ it is possible to prepare a so-called tropenium complex:[5]

$$C_7H_8Mo(CO)_3 + Ø_3C^+BF_4^- \rightarrow C_7H_7Mo(CO)_3^{\oplus}\ BF_4^- + Ø_3CH$$

D. Family VII B

Cotton and Leto[4] have demonstrated the aromatic nature of $CpMn(CO)_3$ by means of Friedel-Crafts acylation of the Cp ring.

Rhenium compounds under investigation have been $(C_5H_5)(C_5H_6)\ Re\ (CO)_2$,[26] $CpRe(CO)_3$,[37] and Cp_2ReH.[27]

E. Family VIII B

The interesting molecule diferrocenyl, $C_5H_5FeC_5H_4 - C_5H_4FeC_5H_5$ [24] has been synthesized. Its infra-red spectrum has played an important role in its characterization.

Hallam and Pauson[28] have reported the synthesis of several indenyl and tetrahydro indenyl iron compounds.

The synthesis of osmocene, $OsCp_2$, has been reported as follows:[11]

$$OsCl_4 + X^{s}S\ NaCp \xrightarrow[\text{dimethyl ether}]{\text{ethylene glycol}} OsCp_2$$

A rather unusual cation has been obtained by Fischer[10] from the reaction of $Hg[Co(CO)_4]_2$ with benzene(trace of $AlCl_3$). The analytical data agree with the composition $(C_6H_6)_3\ Co_3(CO)_2^{\oplus}$ for which a trigonal bipyramidal structure is proposed.

The compound $[C_8H_{10}Co(CO)_2]_2$, dimeric 1,3,6,-cyclooctatriene-cobalt-dicarbonyl, has also been reported by Fischer.[18]

The molecules $(Cp)(CpH)Rh^{I}$ and $(Cp)(CpH)Ir^{I}$ were prepared[22] from the anhydrous metal trichlorides and an excess of KCp plus CpH. Oxidation yields the unipositive cations.

Cp_2Rh^{II} has been obtained in a rather elegant fashion[2] by the nuclear transformation of Cp_2Ru^{104}.

Nickel compounds investigated include $[CpNiCO]_2$,[16] CpNiCOX,[16] $Cp_3Ni_3(CO)_2$,[16] and CpNi - acetylene complexes.[42]

IV. MISCELLANEOUS

The compounds $BeCp_2$ [12] and $ZnCp_2$ [9] have been synthesized, and it has been demonstrated that $ZnCp_2$ is of the "sandwich" type whereas $BeCp_2$ is probably of the σ-bond type.

Reynolds and Wilkinson [38] have recently reported several complexes containing methylcyclopentadiene.

Other significant publications include those on infra-red[23] and proton magnetic resonance spectra[41,32] and dipole moments[19] of aromatic-metal compounds.

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THE USE OF X-RAYS IN DETERMINING THE STRUCTURES OF SOLUTIONS

D. W. Dickerhoof November 24, 1959

I. INTRODUCTION

Some interest has been shown recently in a series of three papers by George W. Brady in which he reports the measurement of the diffraction of x-rays from several aqueous solutions. As a result of these experiments, the following information is reported: the hydration numbers of ions, the distances between molecules and ions in solution, the structures of ionic solutions, and the existence of certain species in solution such as $[FeCl_6]^{-3}$ and Fe_2Cl_6. The unusual nature of some of the conclusions, curiosity as to how they were reached, and their probable validity suggested a deeper study of this topic. Indeed, if the conclusions presented are valid, this method will be a welcome tool for the investigation of the nature and structure of species in solution and for the study of the solution process itself.

II. HISTORY

The diffraction of x-rays by liquids was first postulated by Debye[1] and Ehrenfest[2] in 1915. In fact, a result of this theory was the development of the powder method for solids by Debye and Scherrer.

The next major step was again due to Debye as he introduced the probability function for any given intermolecular distance[3]. Zernicke and Prins[4], bridging the gap between experiment and theory, calculated the diffraction pattern that would result from a particular arrangement of molecules and also showed how to apply Fourier's integral theorem to the determination of the probability function from the observed diffraction pattern. Debye and Menke[5] then applied these results to liquid mercury with good results.

The simple theory was then applied to various elements which could be obtained as liquids[6]. The technique was also applied to pure water and the structure of water was reported[7,8]. Also, some measurements were made on aqueous solutions[9,10,11] (reference 10 in Norwegian).

The most recent work is by Brady[12,13,14]. His conclusions are more far-reaching than those of any previous workers in this field. His work has as yet not undergone a critical review in literature.

III. THE WORK OF BRADY

In order to read this work, it is not necessary to know the theoretical or experimental aspects of the diffraction of x-rays as only a minimum of data and theoretical justification are presented. To understand the principle involved, a recommended text is reference 15 (almost the same symbolism is employed and the final equation is of the same form). Systematic errors are discussed in references 15 and 16.

The experimental data are eventually plotted as the change in the average electron density of the medium as a function of the radial distance from any particular atom in the solution. The final result is the average obtained by considering each atom as the center for this calculation. These curves then show maxima at specific distances which are determined by the various distances of approach of the species in solution.

The technique described in these papers[12,13,14] uses ionic radii and molecular radii in the assignment of the peaks to particular species The area under the curve is used as a measure of the total number of electrons present at a certain distance from a specific ion or molecule. By the assignment of the relative numbers of electrons to different species, the number of ions or molecules involved at each peak is calculated (e.g., hydration numbers). From the combination of all of these, in some cases, the nature of the species present ca be deduced (e.g., $[FeCl_6]^{-3}$ and Fe_2Cl_6).

The major results reported are (1) the hydration number of K^+ i four, of OH^- is six, and of Cl^- around eight or nine (complicated interactions occur, however). (2) The principle species present in 5 molal $FeCl_3$ solution is $[FeCl_6]^{-3}$. At lower concentrations (about 2 molal), the solution is thought to contain 30% Fe_2Cl_6 and 10% $[FeCl_4]^{-1}$. There is no evidence for any aquated iron ion in these solutions.

IV. CRITICISM AND CONCLUSIONS

The validity of the above conclusions can most certainly be questioned. The technical aspects of the work can be criticized for the omission of a detailed description of the exact experimental conditions and the treatment of the data. There are a large number of possible systematic errors[16] in x-ray diffraction work and careful screening of the data is required to eliminate these. The interpretation of the data made no mention of the "statistical geometr involved. There were no sources given for several of the numerical values used and some of the assumptions which were made appear to be justified by the fact that the desired results were obtained. The use of areas under diffraction peaks to obtain any type of informat is seriously discredited by several authors[15,16].

The general conclusion to be reached in regarding x-ray diffra in solution as a physical tool is the statement[17] that the most tha it is now possible to say is that the assumed structure is not inconsistent with the observed data. "It will rarely if ever be poss to make a direct determination of molecular structure."

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IMIDOPHOSPHATES, PREPARATION AND IDENTIFICATION

Dr. Morris L. Nielsen December 1, 1959

I. INTRODUCTION.

The two classes of imidophosphates, containing the $-\overset{|}{\underset{|}{P}}-NH-\overset{|}{\underset{|}{P}}-$ structure, are the linear and the cyclic compounds. Examples of the first are sodium imidodiphosphate, $Na_4P_2O_6NH$, and sodium diimidotriphosphate, $Na_5P_3O_8(NH)_2$; cyclic ones are illustrated by trimetaphosphimic acid, $H_3(PO_2NH)_3$, and its salts.

Formation of P-N bonds is accomplished by the reaction of phosphorus halides or substituted phosphorus halides with ammonia, as in the preparation of phosphoramidates, phosphorodiamidates, phosphorylamide, and the phosphonitrilic halides (1, 2, 3, 4).

A new method of preparing sodium phosphoramidate is by the reaction (5):

$$(NaPO_3)_3 + 3NaNH_2 \rightarrow 3Na_2PO_3NH_2$$

II. LINEAR IMIDOPHOSPHATES.

A. Preparation.

The formation of P-N-P structures has been achieved by condensation through loss of ammonia in the preparation of poly-phosphorylamides (3, 6) and sodium imidodiphosphate (7).

In the synthesis of the latter

$$2(NaO)_2P(O)NH_2 \xrightarrow{\triangle} Na_4P_2O_6NH + NH_3$$

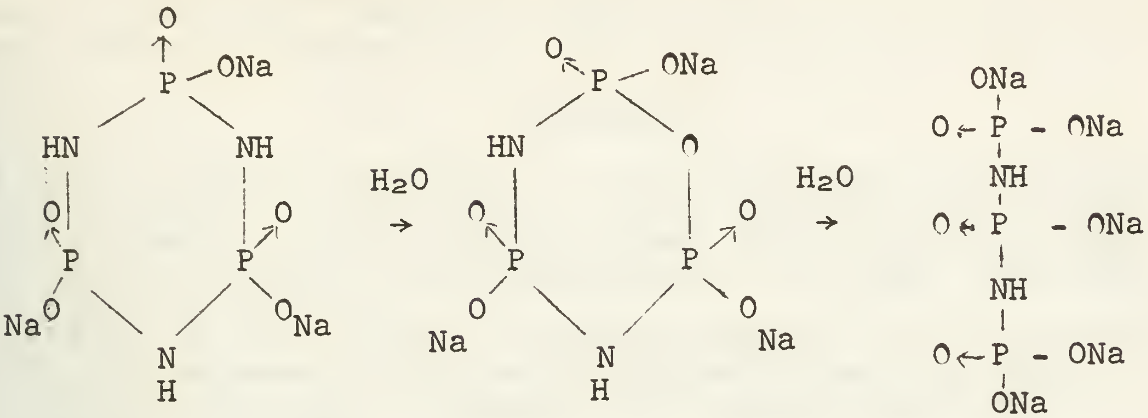
side reactions result in contamination of the product with ortho- and pyrophosphate, as well as with unreacted phosphoramidate due to slowness of the reaction. It has been found that a low-melting flux such as potassium phenoxide accelerates the reaction and results in a better yield (5).

An alternative synthesis is by saponification of diphenyl imidodiphosphoric acid (5) which is prepared by the following series of reactions (8):

$$(\emptyset O)_2P(O)NH_2 \xrightarrow{PCl_5} (\emptyset O)_2P(O)N = PCl_3$$

$$\xrightarrow{H_2O} (\emptyset O)_2P(O)NHP(O)(OH)_2 \xrightarrow[135^\circ]{NaOH} (NaO)_2P(O)NHP(O)(ONa)_2$$

Another method of forming a linear imidophosphate is by opening up a cyclic structure, for example as follows (9):



Older work (10) in which it was presumed that the cyclic "lactam" structure could be easily opened under alkaline conditions and re-cyclicized in acidic conditions is questionable when re-examined by infrared and nuclear magnetic resonance techniques (5).

B. Analysis and Identification.

Since any preparative work requires purification and isolation, methods of analysis and identification are of equal importance to the synthetic work. In the case of phosphorus-nitrogen compounds, elemental analyses are indicative but not conclusive, since nitrogen may be present as ammonium, amido, or imido nitrogen. One method is to rely upon well-crystallized salts for identification by x-ray diffraction (XRD). In the case of the imidodiphosphate, the crystalline yellow salt $Ag_5P_2O_6N$ was used, although a new method for preparing it by using silver acetate crystals had to be developed first. Impurities of octhophosphate, pyrophosphate, and phosphoramidate could be detected by this means. A second method of analysis is by the nuclear magnetic resonance (NMR) of P^{31} (11), in which each species of phosphorus compound exhibits a particular resonance peak depending upon the electronic environment around the phosphorus nucleus. It was found that NMR can detect less than 2% ortho or pyrophosphate in imidodiphosphate.

C. Properties.

The linear imidophosphates are active calcium sequestrants and water-softening agents, much like their oxygen analogs. Diimidotriphosphate can apparently act as a tridentate ligand with calcium, as shown by a model. Solubility of the linear imidophosphates in water is somewhat greater than that of the polyphosphates.

The rate of hydrolysis is markedly related to pH (much faster at pH 10 than at pH 12) and in general greater than for the oxygen analogs.

III. CYCLIC IMIDOPHOSPHATES.

New work in this area includes the preparation of crystalline trimetaphosphimic acid, $H_3(PO_2NH)_3$ by metathesis of the potassium salt with perchloric acid (12). Titration showed this to be a strong acid,

with three replaceable hydrogens. Infrared analysis of the anhydrous potassium and thallium salts revealed sharp bands which were assigned to the N-H structure, changing their position as a result of deuteration to N-D (13). Further evidence of the N-H structure is the preparation of N-chloro salts (14) and the N-ethyl ester (15).

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ADDITION COMPOUNDS OF GALLIUM TRICHLORIDE

Donald A. Wenz December 8, 1959

I. Introduction.

The chemistry of gallium trichloride addition compounds is still relatively unknown. Recent work is beginning to provide needed information on the subject. Some reasons for this interest are the possible use of the trichloride as a Friedel-Crafts reaction catalyst and a comparison of its properties with those of other Group IIIb halides.

Gallium trichloride is a halogen-bridged dimer like aluminum chloride. It can accept a pair of electrons to attain a coordination number of four in an addition compound (1).

The most generally used methods of detecting compound formation have been phase diagram, vapor phase-composition, or conductance studies.

II. Electron-Pair Donors.

A. Halides.

It has been proposed that gallium dichloride could be considered as the addition compound $GaCl_3 \cdot GaCl$ (2), since its structure is $Ga^+[GaCl_4]^-$.

There are a number of alkyl halides that add to gallium trichloride (3,4,5). Methyl, ethyl, and isopropyl chlorides give compounds having $GaCl_3$:donor ratios of 1:1 and 2:1 as shown by phase diagram studies. These compounds are stable at low temperatures, but decompose with evolution of hydrogen chloride at higher temperatures. Stability decreases with increasing branching in the alkyl group.

Methyl bromide, methyl iodide, and triphenylmethyl chloride form only 1:1 addition compounds. The bromide and iodide exchange very slowly with the chlorides of gallium trichloride, indicating that the carbon-halogen bond is still mainly covalent.

B. Acid chlorides.

Phase diagrams of the gallium trichloride-acetyl or benzoyl chloride systems indicate the existence of compounds of 1:1 composition (6). The acetyl chloride compound decomposes on melting, but the benzoyl chloride compound is stable. Conductance measurements show that the latter compound is ionic in the molten state. Because of this, the structure $[RC{=}O]^+[GaCl_4]^-$ has been postulated.

Phosphorus oxytrichloride also forms a 1:1 complex with gallium trichloride (7). Here again, electron pair donation by a chlorine atom is assumed, mainly because of the conducting nature of the liquid complex. However, work on other phosphorus oxytrichloride addition compounds is more conclusive for electron pair donation by the oxygen (10,11).

The compound $GaCl_3 \cdot PCl_3$ is unstable. It exists only as a solid, since on melting it decomposes into its components (8). A bond directly from phosphorus to gallium is postulated.

Phosphorus pentachloride and nitrosyl chloride addition compounds with gallium trichloride have been reported (5,9).

C. Nitrogen- or oxygen-containing donors.

A number of ammoniates of gallium trichloride have been reported. The best characterized of these range from $GaCl_3 \cdot 5NH_3$ to $GaCl_3 \cdot NH_3$ (12,13). The pentammine loses one molecule of ammonia very readily. The other higher ammoniates are more stable, but lose ammonia when heated. The monammine is quite stable. It sublimes without decomposition. Ethylenediamine forms $GaCl_3 \cdot 3en$, which loses all three molecules of amine in a stepwise fashion on heating.

Complexes of 1:1 and 1:2 composition are obtained from the reaction of gallium trichloride with both pyridine and piperidine (14,15). In the molten state these compounds are ionic and conducting. Even though the complexes are ionic, there apparently is some ion-pair interaction because the conductivity of melts of the addition compounds is not as high as it should be for freely moving ions. The 1:2 compounds are less stable than the 1:1 compounds.

When ammonia or trimethyl amine is added to a nitrobenzene solution of gallium trichloride, the conductance rises sharply with small amounts of donor, then levels off as the $GaCl_3$: amine ratio approaches one. No free amine is detected until the ratio is greater than one. On the other hand, when dimethyl ether is added to the gallium trichloride solution, the conductance remains low and fairly constant until it rises shrply at a $GaCl_3$:ether ratio of one. Free ether is present at all times. Thus, apparently the amine compounds are more stable than the ether compounds (16).

A compound of composition $HGaCl_4 \cdot 2R_2O$ has been prepared. It loses ether and hydrogen chloride under high vacuum to give presumably $GaCl_3 \cdot R_2O$ (17).

Benzonitrile, propionitrile, and _p_-nitrotoluene all are reported to form 1:1 addition compounds (18).

III. Conclusion.

The status of knowledge in the field of gallium trichloride addition compound chemistry is that many exist, but practically no good studies have been made to elucidate their structures or the nature of the bonding involved.

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MECHANISM OF NITRATION REACTIONS

C. Y. Fujikawa December 15, 1959

I. INTRODUCTION

Electrophilic substitution has been studied largely in the form of aromatic substitution, where the attack by the substituting agent is on 2p electrons of the conjugated carbon. Since non-bonding 2p electrons of nitrogen and oxygen can participate in such conjugation they should be expected to show properties very similar to the unsaturation 2p electrons of carbon, including general vulnerability to electrophilic substituting agents. For a given substitution of this class, e.g. nitration, the pattern of mechanisms should then be expected to be much the same for C-, N-, and O- substitutions (1).

Nitration has proved to be one of the simpler forms of electrophilic aromatic substitution, because it is dominated by one outstanding mechanism, that involving the nitronium ion. Aromatic nitration through attack of the nitronium ion has been kinetically demonstrated, at first in non-hydroxylic solvents; in hydroxylic but non-aqueous solvents (2,3); and more recently even in the solvent water (4).

The kinetics were followed essentially by standard dilatometry.

II. DILATOMETRY

Dilatometry was first shown to be applicable to the study of reaction kinetics by Knöfler (5). The form of dilatometer used by him, and by the majority of subsequent investigators, consisted essentially of a bulb with a capillary tube at the top and a tap at the bottom for filling. This tap has been a frequent source of trouble, since its presence restricts dilatometry to liquids which do not attack or dissolve tap-grease. Also a minute leak is sufficient to upset the readings. The difficulty is similar if a ground stopper is used in place of the tap, and a rubber stopper is not a satisfactory substitute. Two methods have been tried to overcome this difficulty. One retains the tap but adds an arrangement to protect it. The second method seeks to simplify the apparatus by abolishing the tap. The latter method appears to be the better method.

Early workers had established that the distance, l, travelled by the meniscus of a dilatometer is proportional to the amount by which the reaction under investigation has progressed. The same is found to be true for nitrations, which are accompanied by contractions. The formula for the concentration of reactants at time, t, is then given by $(\underline{l}_{\infty} - \underline{l}_t)D/R$. Where D, the fractional volume change per unit length travelled by the meniscus, is a constant of the dilatometer, and R, the fractional volume change per g.mol. of reaction, is a constant for the reaction.

III. PREVIOUS WORK ON THE KINETICS OF NITRATION

The earliest recorded experiments on this subject are those of Spindler (6), who examined the nitration of benzene and some of its simpler derivatives with various amounts of nitric acid at various temperatures. No solvent was used, and hence the reaction mixtures were heterogeneous. No rate constants were obtained. The first to obtain velocity constants was Martinsen (7), who employed nitric acid in sulfuric acid. The rate of nitration of benzene and other compounds by means of nitric acid in acetic anhydride was first studied by Wibaut (8), and later by Cohen (9). The latest published investigations along these lines are those of Ingold and coworkers (1-3, 10-13).

IV. MECHANISM OF NITRATION

The mechanism may be expressed in the following scheme:

$$HNO_3 + HNO_3 \underset{-1}{\overset{+1}{\rightleftharpoons}} H_2NO_3^+ + NO_3^- \qquad \text{(fast)}$$

$$H_2NO_3^+ \underset{-2}{\overset{+2}{\rightleftharpoons}} NO_2^+ + H_2O \qquad \text{(slow)}$$

$$NO_2^+ + XH \underset{3}{\rightarrow} XH{\cdot}NO_2^+ \qquad \text{(slow)}$$

$$XH{\cdot}NO_2^+ + NO_3^- \underset{4}{\rightarrow} X{\cdot}NO_2 + HNO_3 \quad \text{(fast)}$$

Nitric acid is in large, and substantially constant, concentration. The nitronium ion is formed in two steps, of which the former, a protonation, is always fast. Then the substitution in the substrate goes in two steps, of which the latter, a deprotonation, is always fast. The intermediate steps, 2 and 3, are slow. With a sufficient concentration of a sufficiently reactive substrate, and in a not-too-aqueous medium, step 3 prevails over step -2, so that the nitronium ion reacts, as fast as it is formed, with the substrate, and the measured rate is the rate of its formation in step +2. As long as the nitronium ions are trapped almost wholly by the substrate, the measured rate must be independent of the concentration and nature of the latter: the reaction will be of zero order in the substrate.

The other limiting situation is that in which the substrate is so unreactive, or so dilute, or the medium is so aqueous, that step -2 prevails over step 3 in the consumption of nitronium ion. The reaction will now be of the first order in the substrate.

V. EXISTENCE OF THE NITRONIUM ION

Nitration through the nitronium ion, NO_2^+, is an old theory, having been proposed by Euler in 1903 (14) and frequently supported since that date, but it was not established, and even the existence of the ion was not conclusively demonstrated, until 1946 (15).

The existence of the nitronium ion has been proved in four ways (16). Its formation in large concentrations in certain solutions, notably in sulfuric acid solution, has been demonstrated (a) by cryoscopic measurements (17) and (b) by spectroscopic studies on such solutions (18). Its identification as the cationic unit in ionic crystals has been established (c) by the preparation and spectroscopic

VI. [illegible] WORK ON THE [illegible] REACTION

The earliest important investigations by [illegible] are those of [illegible] (1), who [illegible] the [illegible] of [illegible] and [illegible] of the [illegible] (15) [illegible] amounts of [illegible] at various temperatures. He [illegible] and found the [illegible] mixture [illegible]. [illegible] (7) [illegible] (8) [illegible] (9). [illegible] along these lines [illegible].

V. MECHANISM OF NITRATION

The nitration [illegible] is represented in the following scheme:

[illegible]

[illegible] (fast)

[illegible] (slow)

[illegible] (fast)

Nitric acid [illegible] [illegible]. [illegible]

[illegible]

2. [illegible] OF THE NITRONIUM ION

[illegible] (1903) (7) [illegible] (Eq. 15).

The [illegible] of the [illegible] (16). [illegible] (17) [illegible] solutions [illegible].

study, of crystalline nitronium salts (19) and (d) by x-ray analyses of certain nitronium salts (20).

VI. C-, N-, O- NITRATION

Detailed study of aromatic nitration in nitromethane has been made. Nitric acid was always employed in large, effectively constant excess. The nitration of benzene was a reaction of zero order. The nitrations of toluene and of ethylbenzene were also reactions of zero order, with absolute rates always equal to each other and to the rate of nitration of benzene for the same condition (2).

The N-nitrations of secondary amines by nitric acid in constant excess in nitromethane of not-too-high water content are of zero order. Small additions of sulfuric acid increase, of nitrate ions reduce, and of water do not change, the zero-order rate. But larger additions of water increase the rate, with maintenance of the zero-order form, and still larger ones change the kinetics to first-order form. These effects fully establish the nitronium ion mechanism for N-nitration. Measurements have been made on the zero-order N-nitrations of N-methyl-, N-ethyl-, N-n-propyl-, and N-n-butyl-trinitroaniline (1).

The O-nitrations of methyl alcohol, p-nitrobenzyl alcohol, ethylene glycol, trimethylene glycol, and also glycerol with respect to its primary hydroxyl groups, are of zero order and identical in absolute rate with one another and with the N-nitrations of N-methyl trinitroaniline and with the C-nitrations of benzenoid hydrocarbons under the same conditions. The effects upon addition of sulfuric acid, nitrate ion, and water were the same as in the previous case (21).

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THE ROLE OF METAL IONS IN ENZYME ACTIVITY

Soter G. Kokalis January 5, 1960

I. CHARACTERISTIC OF AN ENZYME:

A. Introduction

Life is a manifestation of catalysis by means of enzymes; without these catalysts, there could no longer be life! Thus, the study of enzyme activity is man's way of understanding the nature of his very existence. This report will deal with the work accomplished in elucidation of the role metal ions play in enzymatic catalysis. At least six hundred fifty different enzymes have been characterized, which may make one realize what confusion could easily result if systematic classification does not prevail (8a).

B. Classification

Enzymes may be classified in several fashions. Thus, enzymes are categorized on the basis of the type of general reaction catalyzed, e.g., oxidation with its oxidases, hydrolysis with its peptidases, etc. Another method employs the strength of the bonding of the metal ion to the protein portion of the enzyme (2). This includes material ranging from metalloenzymes, with a firm metal-protein bond, to the metal enzymes, which have very loose bonding of metal ion to protein. Empirical formula have been developed for some well characterized metalloenzymes (1).

The concept of metal-ion activation of enzymes has been recently discussed (3). It serves as a foundation for developing an understanding of how metal ions rule life--from the iron of hemoglobin to the magnesium of chlorophyll (5). Some vitamins may even be considered as metalloenzymes as is the case with vitamin B_{12}, a cobalt(III) enzyme involving coordination by a cyclic imine system (1).

C. The Chemical Nature of Enzymes.

How does one know a metal ion is present and necessary for enzyme action? Since trace amounts of metal are required by enzymes, e.g., one iron atom for a molecule of liver catalase (Mol. wt. 225,000) sensitive microanalysis or emission spectroscopy must be employed to detect the metal ion. After inactivation of an enzyme by dialysis with cyanide or sulfide ions, cysteine, phosphate, or other metal complexing agents, addition of metal ions may serve to reactivate the enzyme, thus indicating a metal requirement. If loss of metal ion does not affect activity, the enzyme can be classified as a non-metalloenzyme (13). Some recent studies have even employed EDTA to reduce enzyme activity by 80% (12).

Ionic and covalent bonds are used to coordinate metal ion to various ligand groups of the protein and substrate molecules (6). Various ligands permit the coordinated metal ion to serve as the bridge for the enzyme substrate complex (6). The ability of Mg^{++} to complex with organic phosphates is responsible for its utilization by A.T.P.-ase, which is necessary for the energy transfer in living systems. Magnesium ion chelates with the pyrophosphate portion of the substrate and hydrolysis removes the terminal phosphate with a resulting ΔF of 11,500 cal./mole, useful for endoergic reactions.

Rates of enzyme reactions have been studied and have been found to be dependent on optimum temperature; pH; concentration of substrate, metal ion, inhibitor, and product; and ionic strength of the media. Thus, a means of distinguishing enzymes is readily available in these various determinants of maximum enzyme activity.

Enzymes are quite specific catalysts in relationship to the substrate. There is a chemical bond specificity as evidenced in enzymes such as the esterases and peptidoses that split only esteric or peptide linkages. A report by E. Smith reveals the aspect of stereochemical specificity (4). He shows how the substitution of a minor group on a substrate can be a major deterrent to enzyme action. A definite spatial requirement is imposed by the enzyme on its substrate. The geometry of the coordinated metal ion can be of importance also.

II. MODEL SYSTEMS AS A ROUTE TO ENZYME MECHANISMS:

A. Organic Mechanism of Catalysis

Most chemical reactions catalyzed by enzymes are susceptible to catalysis by simpler organic or inorganic reagents. Once the mechanisms of catalytic processes are fully understood, the development of enzymatic mechanisms will be facilitated. Catalysis by a stable intermediate, with a corresponding lowering of activation energy, seems to be the way an enzyme increases the rate of reaction.

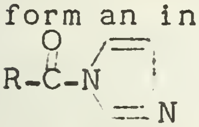
B. Examples of Model Systems.

On the basis of kinetic studies the mechanism for the alkaline hydrolysis of esters has been found by Ingold (18) to be the following:

$$R-\overset{O}{\overset{\|}{C}}-OR^1 + OH^{-1} \underset{fast}{\overset{slow}{\rightleftharpoons}} \left[R-\overset{O^{\ominus}}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-OR^1 \right] \underset{slow}{\overset{fast}{\rightleftharpoons}} R^1O^{\ominus} + R-\overset{O}{\overset{\|}{C}}-OH.$$

$$R^1O^{\ominus} + RCOOH \xrightarrow{fast} R^1OH + RCOO^{\ominus} .$$

Recently, studies were made of ester hydrolysis utilizing imidazole as the basic catalyst (15,16). In the mechanism, it was found that the ternary nitrogen bonded to the carbonyl carbon, as does OH^-, to form an intermediate which decomposes into $R^1O^{\ominus}$ and the species



, with a definite absorption at 245 mm. It is unique that chymotrypsin, the enzyme for ester hydrolysis, also possesses an imidazole ring. Isotope exchange has verified the fact that the enzyme forms the acylated species, $R-\overset{O}{\overset{\|}{C}}-Enzyme$. Thus, a ligand portion vital to enzyme operation may be verified by the model system study.

The mechanism of amino acid transamination has been explored by E. Snell (17) in a model system utilizing a polyvalent metal ion, pyridoxal, and glutamic acid. The mechanism employs Al^{+3} to stabilize a Schiff base as an intermediate, as well as to remove electron density from the C-N bond to be hydrolyzed.

Isotope and kinetic studies can be very helpful in developing a mechanism, yet one must keep in mind that this is only an attempt to draw on analogy between the enzyme and the structure of the intermediate. Many enzymatic reactions do not follow the mechanism of the non-enzymatic catalysis.

III. ENZYME SYSTEMS

A. Experimental Procedures

Some important hints about laboratory manipulation of enzymes and solutions of enzymes have been indicated by Dixon and Webb (8c). These include operating at $0^{o}C$ if possible, avoiding the drying of material at room temperature, and cautiously adding OH^- or H_3O^+ ions to the enzyme in solution. Purity of enzymes can be easily determined by the velocity of the reaction in transformation of a substrate. Kinetics has been found very useful in studying the activated complex. The particular rate law can be obtained by following the reaction by a host of physical or chemical methods (8b). Spectrophotometry, polarimetry, manometry, chromatography, or periodic microchemical analysis can serve to give kinetic data. "The development of a mathematical picture of atomic and electronic rearrangements at each step of the process is possible!" (7). R. A. Alberty explains the role of kinetics in revealing the activated complex--the vital intermediate of substrate and enzyme by metal-ion intervention (9).

B. The Enzyme-Metal-Substrate Complex (E.M.S.)

Inhibitors are of great value in elucidating the exact atomic configuration at the active site of the enzyme. Drugs (alkaloids are enzyme inhibitors, and many other molecules are useful in this respect, e.g., metal poisons (CN^-, $S^=$, N_3^-, CO), heavy metal ions (Ag^+, Pb^{++}, Hg^{++} all serve to precipitate the protein), and organic phosphorus compounds of the general structure, $R_2\overset{}{\underset{O}{P}}X$ ($X=F^-$, CN^-, ), which result in a stable phosphorylated enzyme.

As E. Frieden points out in his discussion of the E.M.S. complex, color changes can serve as a qualitative indication of complex formation (19).

Quantitative measurement of the complex employs spectrophotometry, where the shift in wavelength can be followed for all the components. Dialysis of the enzyme with an inhibitor can result in a complex of the proper stoichiometry and thus can reveal the number of active sites per enzyme. In that an equilibrium is established with no reaction products appearing, the K_{eq} can be determined at different temperatures. The ΔH_{form} of the complex is then easily obtained.

A recent method employs "crossing-paper electrophoresis" to detect E.M.S. complexes (20).

The metal ion may be responsible for one or several of the following functions in the formation and reaction of the E.M.S. complex:

1) Complexing with the substrate to produce the correct configuration for bonding with the enzyme.
2) Complexing with the enzyme to obtain its structure in an active configuration to bond with substrate.
3) Behavior as a Lewis Acid and consequent reduction of electron density in the bond to be split; or attraction of OH^- ions that can attack the weakened bond.
4) Removal of an inhibitor on the enzyme by complex formation or precipitation, there liberating an active enzyme.
5) Displacement of ineffective ions from the active center of the enzyme.
6) Serving as an electron acceptor and donor bridge in redox reactions; electron spin resonance has revealed the valency change of copper in fungal laccase (14).

The pH dependence curves of enzymatic activity have been used to determine the dissociation constants of groups involved in the catalytic mechanism (21). Thus a means is available to establish the structure of the activated complex by knowing the active ligand ingredients.

C. Xanthine Oxidose

An excellent survey has been made of the oxidative functions of metalloflavon enzymes (10). The vital components of xanthine oxidase system include flavin adenine dinucleotide (FAD), iron as hematin, and loosely held molybdenum. The atomic ratio of Mo/Fe/F.A.D. per mole of protein (mol. wt. 230,000) is 1/4/1 (9). Xanthine, purines, diphosphopyridine nucleotide, and aldehydes are oxidized by this enzyme. Electron spin resonance has verified a semiquinoid free radical (F.A.D.) as an intermediate, indicating that the unpaired electron is smeared over the flavin molecule with the metal ions serving as bridges for electrons to acceptors (22, 23). Although iron(II) of heme carries oxygen without becoming oxidized, the iron(II) of oxidase is oxidized by the FAD radical.

IV. CONCLUSION

A. Areas of Profitable Investigation by Inorganic Chemists:

With the host of physical methods available, a new era is opening in enzyme studies. Metal chelate data must be compiled in the physiological range of pH and temperature. Studies of mixed chelates of the type $\dot{M}(NH_2R)_x(PO_3R)_y$, etc. would give valuable insight into the enzyme-substrate bonding by metal ions. X-ray determination of enzyme-metal structures is sorely needed, but great difficulties will need to be overcome owing to the complexity of the protein portion of the structure (24).

A bit more success was attained recently when simple polypeptides were studied by x-rays in the model system: Cu^{II} and biuret (25). More x-ray study is needed on metal-substrate complexes using amino acids, peptides, and organic phosphates as substrates. Complexes of pyrrole and its derivatives with iron, copper, and cobalt could provide an answer to the synthesis of the vital enzymes of respiration and carbohydrate metabolism, i.e., hemoglobin, oxidase, and chlorophyll.

B. The Potential of the Research Endeavors Relating to Enzyme Mechanisms.

Everything we do is done with some enzymatic process; life is a system of cooperating enzymes. Understanding enzyme mechanism could lead ultimately to the mechanism of diseases of a metabolic character, and perhaps even to cancer, which is considered to be instigated by enzymes that become less specific in time and thus promote random or tumor growth. That inorganic chemists are realizing the important role of the metal ions in biochemical processes is evidenced by the pending Inorganic Division Symposium on this topic at the 138th ACS meeting to be held at New York City, September 11-16, 1960.

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DETECTION OF IONS BY THE METHOD OF CHARLOT

Samir K. Thabet January 12, 1960

Dr. G. Charlot is Professor of Analytical Chemistry at the Ecole Supérieure de Physique et d Chimie, Paris. The method of Qualitative Inorganic Analysis which he developed aims at detecting ions without resorting to the classical methods of separation into groups and without using H_2S. Each ion in a mixture of ions can be identified by carrying simple tests on the mother solution. The method makes use of different means of characterization and detection such as pH control, complex formation, adjustment of redox potential, solvent extraction, precipitation and fluorescence. It is similar in many ways to the methods used in colorimetry.

The method has been the subject of controversies and has met with considerable opposition from chemistry teachers. Recently, however, it seems that the method is gaining recognition and a number of European institutions are at present using it.

Charlot's method presents various advantages both practically and pedagogically, but certain improvements and refinements are still desirable. The method was first published by Masson, Paris, in 1942. The English text "Qualitative Inorganic Analysis - A New Physico-Chemical Approach" was translated by Dr. R. C. Murray and was published in 1954 by Methuen, London, and Wiley, New York. It is divided into three parts. In Part I, the general properties of compounds in solution are described and the method of expressing these properties in quantitative terms are developed. Reactions involving the exchange of electrons (oxidants and reductants) of ions and molecules (complexes) and of protons (acids and bases) are discussed and it is shown that all these cases can be treated in a similar manner using the same equations.

In Part II, the individual properties of the more important ions and compounds and their detection and characterization are described. No distinction is drawn between familiar and less familiar elements.

In Part III, the details of the analytical procedures are described. A more recent French edition introduces a number of improvements, this, however, is not yet available in English.

ROLL CALL

PARAMAGNETIC SUSCEPTIBILITIES BY THE NMR METHOD

John G. Verkade January 19, 1960

A method of measuring the gram susceptibility of a paramagnetic substance in solution was discussed (1). Due to the additional field from the paramagnetic material imposed upon the standard in the NMR tube, the proton resonance of that standard will appear at a higher field than the standard contained in the capillary tube.

A formula was given which affords the gram susceptibility of the paramagnetic compound directly from a knowledge of the frequency separation of the two standard peaks, the frequency at which proton resonance is being studied, the concentration of the paramagnetic compound in solution, the gram susceptibility of the solvent, and the densities of the solvent and solution.

The solvents may be organic or aqueous, and the standards employed in the solvents (2% concentration) include tertiary butanol, acetone, and tetramethyl silane. Besides being accurate to 0.4 cgs unit in gram susceptibility, the method has the advantage that only a very small amount of substance is required (0.2 ml of 0.01 to 0.1 molar solution).

Reference

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THE USE OF THERMISTORS IN MOLECULAR WEIGHT MEASUREMENTS

Dean Dickerhoof January 19, 1960

A thermistor is a semiconducting material made of sintered transition metal oxides (e.g. $NiO + Mn_2O_3$), which exhibits a large, negative temperature coefficient of resistance. A relatively simple Wheatstone bridge circuit using a thermistor as one of the resistances is a very accurate temperature sensing device, especially for the small differences encountered in boiling point or freezing point changes. This permits molecular weight determinations to be made on solutes with low solubilities and allows more dilute solutions to be employed further minimizing possible solute-solvent interactions. By obtaining " matched" thermistors which have the same temperature dependence, the second thermistor can be placed in the opposite arm of the bridge circuit so that one thermistor is in the pure solvent and the second one is in the solution. Temperature differences on the order of 10^{-4} can be detected. Thermistors are very small, rugged, and relatively cheap and deserve consideration in any cryoscopic or ebulliometric determination of molecular weight.

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THE HYDROLYSIS OF DIPHOSPHORUS TETRAIODIDE

James E. Huheey January 19, 1960

Diphosphorus tetraiodide was hydrolyzed with a large excess of water under various experimental conditions. (1) The hydrolysis products were found to have a strong reducing action against iodine in acid solution. When oxidized in sodium bicarbonate solution and then acidified, no further iodine consumption was noted. The species responsible for reduction of iodine in acid solution was found to be easily oxidized by atmospheric oxygen and when precipitated as the barium salt, it remained insoluble in 2N acetic acid. From these experimental data it is possible to eliminate the following phosphorus acids as responsible for the iodine consumption of acid: Hypophosphorous, phosphorous, pyrophosphorous, hypophosphoric, and phosphoric. Furthermore, when the components of the hydrolysis were separated by paper chromatography, using care to prevent air oxidation, the acid in question produced a unique fleck in the region of pyrophosphorous acid. On the basis of the above data the following structure was suggested:

```
     H   H
     ↑   |
HO - P - P - OH
     ↓   ↓
     O   O
```

Although no hypophosphorous acid was shown to be present, various amounts of phosphorous acid, phosphoric acid, hypophosphoric acid, hydroiodic acid, and phosphine were found in the hydrolysate.

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HEXASULFANEMONOSULFONIC ACID, $H_2S_7O_3$, AND TETRADECATHIONIC ACID, $H_2S_{14}O_6$

R. E. Eibeck

January 19, 1960

In 1957, a new class of compounds, the sulfanemonosulfonic acids, was prepared by the reaction of sulfur trioxide with sulfanes.

$$H_2S_x + SO_3 \rightarrow H_2S_{x-1}O_3$$

Among the known compounds of this type, i.e. those in which x + 1 = 2, 3, 4, 5, 6, the stability decreases sharply with increasing length of the sulfur chain in the molecule. Schmidt and Dersin (1) have raised a question as to whether higher homologs in the series are stable.

The compound hexasulfane, H_2S_6, became available through the reaction of S_2Cl_2 with H_2S_2:

$$2H_2S_2 + S_2Cl_2 \rightarrow H_2S_6 + 2HCl$$

Hexasulfane reacts with sulfur trioxide to form $H_2S_7O_3$, hexasulfanemonosulfonic acid,

$$H_2S_6 + SO_3 \rightarrow H_2S_7O_3$$

Hexasulfanemonosulfonic acid has the same general properties as its lower homologs, but it is considerably less stable.

In a non-aqueous solvent, chlorine will oxidize $H_2S_7O_3$ to $H_2S_{14}O_6$, tetradecathionic acid,

$$2H_2S_7O_3 + Cl_2 \rightarrow H_2S_{14}O_6 + 2HCl$$

Reference

1. M. Schmidt and H.. Dersin, Z. Naturforsch., 14b, 735 (1959).

ROLL CALL

THE SOLUBILITY OF ALKALI METALS IN ETHERS

Therald Moeller February 23, 1960

Although the dissolution of alkali metals in liquid ammonia and the lower aliphatic amines is a familiar phenomenon and one commonly discussed in relationship to both the nature of the metallic state and the characteristics of non-aqueous solutions, it is less well known that similar solutions result in water, in the lower alcohols, and in a variety of ethers (1). A comprehensive study (2) involving fifteen ethers and one aminoether has shown that potassium, either as such or as the sodium-potassium eutectic, dissolves to the extent of roughly 10^{-4} g. atom/liter in such solvents. The characteristically blue solutions obtained are stable in contact with excess metal and in the absence of air. They are decolorized immediately in contact with air. Filtered solutions decolorize slowly, presumably because of reaction with dissolved metal. Comparable solutions were not obtained with lithium, sodium, or calcium, but it is reasonable to assume that they would result with rubidium or cesium. Of the various factors that might enhance solubility, it is believed that those relating to the solvation of the potassium ion are most significant. Among these are the number of donor oxygen atoms in the ether, the size of potential chelate rings in the solvated cation, and steric interactions of the donor oxygen atoms with close substituents in the ether structure. The best solvents are those with more than one oxygen atom in such arrangement that 5-membered rings can result.

These blue solutions all absorb strongly at 7000 A. Such measurements as have been made indicate them to be diamagnetic. Since with liquid ammonia solutions of the alkali metals absorption at $\sim$ 6500 Å. is associated with diamagnetism and the presence of paired electrons trapped in cavities, it is believed that the ether solutions of potassium are comparable. Absorption at $\sim$15000 Å., which is associated with unpaired trapped electrons in liquid ammonia solutions, was not detected for ether solutions.

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SYNTHESIS OF SILYLPHOSPHINES

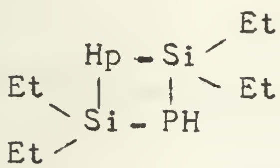
D. B. Sowerby February 23, 1960

Compounds containing direct silicon-phosphorus bonds have been prepared (1) by the reaction of a mixture of the various lithium phosphides (PH_2Li, $PHLi_2$, PLi_3) with trimethylchlorosilane in ether solution, e.g.,

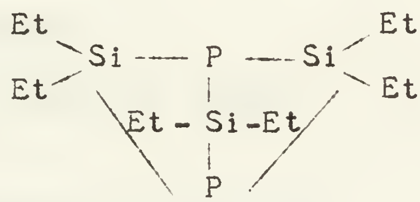
$$Me_3SiCl + PH_2Li \rightarrow Me_3SiPH_2 + LiCl \quad \text{etc.}$$

Filtration of the lithium chloride leaves a complex mixture, which can be fractionated to yield samples of the mono- , bis- and tris- (trimethylsilyl) phosphines. All three products are inflammable in air and sensitive to moisture and oxygen. Tris-(trimethylsilyl) phosphine shows remarkable behavior on oxidation with N_2O_4; the product is not the expected phosphine oxide but the corresponding phosphate.

The reaction of diethyldichlorosilane with the lithium phosphide mixture yields two cyclic compounds (I and II) — the first to be isolated involving four-membered silicon-phosphorus rings.



I



II

The compounds are readily isolated and are thermally stable. Although compounds I and II have been named systematically, e.g., for compound II, 2,2,4,4,5,5, - hexaethyl - 1,3 - diphospha - 2,4,5 - trisilabicyclo- (1.1.1) pentane, a new approach to the nomenclature of such inorganic cyclic compounds seems desirable.

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MOLECULAR COMPLEXES BETWEEN IODINE AND N,N-DIMETHYLANILINE DERIVATIVES

R. S. Drago February 23, 1960

The equilibrium constants, free energy change ΔF^{o} enthalpy change ΔH^{o}, and entropy change ΔS^{o} of formation were determined for iodine complexes with N,N-dimethylaniline and its methyl derivatives. These data were obtained by using ultraviolet spectroscopy and working in dilute n-heptane solutions of the reagents. The following results were obtained.

Base	$-\Delta H$(kcal./mole)	$-\Delta S$(e.u.)
N,N-dimethylaniline (I)	8.2 ± 0.3	21.6 ± 0.6
N,N-dimethyl-p-toluidine (II)	8.3 ± 0.2	20.8 ± 0.4
N,N-dimethyl-o-toluidine (III)	2.3 ± 0.5	6.2 ± 1.0
N,N-dimethyl-2,6-xylidine (IV)	1.7 ± 0.3	3.6 ± 0.6

It is proposed that in compounds III and IV the phenyl group is forced into a position causing it to exert a steric repulsion toward the incoming iodine molecule.

Reference

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TETRACHLOROMETALLATE(II) COMPLEXES

T. S. Piper February 23, 1960

The preparation, structure, and magnetism of tetrachlorometallate (II) complex ions have been reported (1). The article also reviews previous work.

The large cations $\emptyset_3MeAs^+$ and Et_4N^+ were used to stabilize the anions in crystals. Crystals of $(\emptyset_3MeAs)_2MCl_4$ were cubic ($PZ_13, Z = 4$), with MCl_4^{-2} ions at sites of symmetry C_3. Thus the ions are tetrahedral or slightly distorted with three bond lengths different from the fourth.

Magnetic studies confirmed the nearly tetrahedral configurations. Large orbital contributions increased the magnetic moments much above the spin-only values:

Ion	u	u(spin-only)
NiX_4^{2-}	3.9-3.5 B.M.	2.83 B.M.
CoX_4^{2-}	4.7-4.9	3.85
MnX_4^{2-}	5.9	5.9
$CuCl_4^{2-}$	1.91	1.73

The magnetic moment expected for $CuCl_4^{2-}$, if it were perfectly tetrahedral, is 2.2 B.M. Thus there is some distortion from tetrahedral symmetry as required by the Jahn-Teller theorem.

Reference

1. N. S. Gill and R. S. Nyholm, J. Chem. Soc., 1959, 3997.

THE BIOLOGICAL ROLE OF PHOSPHORUS

T. L. Brown February 23, 1960

In a recent article which reports the free energy and enthalpy of hydrolysis of pyrophosphate (1), Van Wazer and co-workers have discussed the role of phosphorus in the chemistry of living systems. Those properties of the phosphorus atom which are important in its chemistry in living systems (it is present as phosphate) include:

a. availability of d orbitals for formation of stable intermediates.

b. solubility in aqueous media

c. oxidation-reduction stability

d. slow rate of uncatalyzed hydrolysis of condensed phosphates

e. favorable values of ΔF for hydrolysis equilibria.

The authors minimize the importance of the last factor. An analysis of the problem however, would seem to show that this favorable energy range for the hydrolysis reactions is the only factor which unequivocally rules out other condensed systems as possible counterparts of the phosphates in living systems.

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ALKYL AND ARYL DERIVATIVES OF TRANSITION METALS

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March 22, 1960

I. INTRODUCTION

The compounds which form the subject of this lecture are theoretically derived from hydrocarbons by replacing an atom of hydrogen by its equivalent of a transition metal. Such compounds of the non-transition metals have been known for over 100 years. Normally they have the formula $(MR_{\underline{n}})_{\underline{m}}$ or $(MX_{\underline{y}}R_{\underline{z}})_{\underline{m}}$, where R is an organic radical, x is an anionic radical (usually a halogen), and $\underline{y} + \underline{z} = \underline{n}$, the valency of the metal. If M has two valencies, n is usually the higher valency. These compounds are generally thermally stable, but very reactive. Many inflame in air and react violently with water and acid. Examples are $ZnEt_2$ and $(AlMe_3)_2$.

The transition elements do not appear to form stable organo-metallic compounds of these types. There have been many attempts to prepare them in the classical manner, but, excepting a few compounds of titanium(IV), platinum(IV), and gold(III), none was satisfactorily characterized. The position in 1955, as summarized by Cotton (1), included one or more well established compound for titanium, chromium, and platinum; some positive results requiring confirmation for niobium, tantalum, molydenum, tungsten, and rhenium; and no results or inconclusive results for the other elements. The compounds of chromium mentioned are now known to be complex chromium(I) species containing diphenyl and not phenyl drivatives of chromium(V) as previously believed. Although only five years ago it appeared that no more than a few unstable alkyl and aryl compounds of the transition elements might ever be prepared, more recent work has shown the existence of new and remarkably stable types of compounds.

These are complex compounds in which the transition metal is bound to a number of ligands in addition to the alkyl or aryl radicals. They have the general formula $[MX_{y}R_{z}L_{n}]$, where X is an anionic ligand, R is the alkyl or aryl radical attached to the metal, and L is an uncharged ligand. Many of these, and certainly all of the most stable, are diamagnetic. The ligands L, which give the best stabilization, are those which cause electron pairing in the complex molecule. The cyclopentadienyl anion, carbon monoxide, nitric oxide, tertiary phosphines and tertiary arsines are the ones most commonly used. The metal atom in these complexes usually has the effective atomic number of the next inert gas or has only a few electrons less than the next inert gas. The non-bonding d-orbitals are thus occupied by at least one electron each, but most commonly by two electrons each. The only exceptions are the simple organo-titanium compounds $[TiMe_4]$,$[TiCl_3R]$, and $[TiCl_2R_2]$ (2,3). These are of the same type as those obtained from the non-transition metals but are thermally much less stable.

II. METHODS OF PREPARATION

Major methods include

A. Reaction of organo-lithium compounds or Grignard reagents with suitable halo-complexes of the transition metals, e.g. ,

$[Ti(C_5H_5)_2Cl_2] + 2\ RLi \rightarrow [Ti(C_5H_5)_2R_2] + 2\ LiCl$ (4,5)

$[PtCl_2(PR_3)_2] + R'MgX \rightarrow [PtClR'(PR_3)_2] + MgXCl$ (6)

B. Reaction of alkyl halides with sodium salts of suitable complexes, e.g.,

$Na[Mo(C_5H_5)(CO)_3] + RI \rightarrow [MoR(C_5H_5)(CO)_3] + NaI$ (5)

If a choice between A and B exists, B gives the better yield.

Minor methods include

C. Reaction of diazomethane with a complex hydride (5,7),e.g.,

$[MnH(CO)_5] + CH_2N_2 \rightarrow [Mn(CH_3)(CO)_5] + N_2$ (8)

The method is limited to the synthesis of methyl derivatives. Not all complex hydrides react, however, and yields are poor.

D. Reaction of an alkyl halide with a complex containing the metal in a low oxidation state, e.g.,

$[Pt(PPh_3)_4] + 3\ MeI \rightarrow [PtIMe(PPh_3)_2] + 2[PMePh_3]I$

Methyl iodide gives better yields than the higher alkyl iodides. The reaction is interesting because it produces an organo-transition metal compound without use of a more reactive organo-metallic derivative.

III. TYPES OF ALKYL AND ARYL COMPLEXES

These are conveniently classified according to the stabilizing ligands.

A. Cyclopentadienyl Complexes

Such species were among the earliest to be described (4). Reaction A (above) is a useful method of synthesis. An interesting exception to this reaction is found when methyl cyclopentadienylmanganese chloride is treated with phenyl magnesium bromide and the product hydrolyzed (9). Methylcyclopentadienylbenzenemanganese(I) is obtained rather than methylcyclopentadienylphenylmanganese(II).

B. Carbonyl Complexes

Carbon monoxide is especially effective in stabilizing alkyl and aryl derivatives of manganese (8,10) and rhenium(II) of the type $[MR(CO)_5]$. The alkyl derivatives are best prepared by the reaction of a sodium salt $Na[M(CO)_5]$ with an alkyl halide. The manganese compounds show an interesting reversible conversion to aryl derivatives of the metal (12), as

$$[MnR(CO)_5] \underset{\text{pyrolysis}}{\overset{\text{CO, 500 psi, 20oC.}}{\rightleftarrows}} [Mn(COR)(CO)_5]$$

Treatment of $Na[Mn(CO)_5]$ with benzoyl chloride gives $[Mn(COPh)(CO)_5]$, which loses carbon monoxide when heated and gives $[MnPh(CO)_5]$.

C. Mixed Cyclopentadienyl-Carbonyl-Nitrosyl Complexes

These compounds have the general formula $[MR(C_5H_5)(CO)_x(NO)_y]$. They are prepared either from the corresponding halide by reaction with a Grignard reagent or, in the case of alkyl derivatives, by reaction of the sodium salt of the hydride with an alkyl halide (5). Known compounds include $[FeR(C_5H_5)(CO)_2]$ (R=Me,Et,Ph); $[CrR(C_5H_5)(NO)_2]$(R=Me,Et,Ph,C_5H_5, CH_2Cl); $[MR(C_5H_5)(CO)_3]$(M=Cr,R=Me; M=Mo,R=Me,Et,Pr; M=W,R=Me,Et).

D. Organic Phosphines, Arsines, and Sulfides

Known compounds stabilized by tertiary phosphines include those of platinum (6,13), palladium (14), nickel (15), cobalt (15), and osmium (16). All correspond to the general formula $[MX_mR_n(\text{phosphine})_p]$, where n is usually 1 or 2, m is 1 or 0, and p represents the number of groups needed to complete the coordination shell. Arsines and sulfides are less effective than phosphines. These compounds are obtained from the corresponding halo complexes by Reaction A except for the ruthenium and osmium compounds, where reactions of dihalo complexes with aluminum

methyl or ethyl are useful. Many of these compounds have remarkably high thermal stabilities, and some, e.g., cis-[$PtMe_2(PMe_3)_2$] and trans-[$NiBr(Mes)(PEt_3)_2$], are quite stable to air and acids.

Chromium yields some unique compounds. Thus reaction between benzyl chloride and chromium(II) perchlorate in water yields (17) [$Cr(CH_2Ph)(H_2O)_5]^{2+}$ and [$Cr(CHCl_2)(H_2O)_5]^{2+}$ results from chloroform (18). These compounds are surprisingly stable but do hydrolyze slowly in water. Phenylchromium complexes, [$CrPh_3(THF)_3$], result in reactions of the chloride with a phenyl Grignard in tetrahydrofuran (THF)(19). Lithium phenyl yields $Li_3[CrPh_6]$ (20).

IV. STABILITY CONSIDERATIONS

The instability of simple transition metal complexes of the type $[MX_yR_z]_m$ may be due to the ease of promotion of electrons from relatively high-energy filled d-orbitals into antibonding σ-orbitals of the carbon-metal bond or, if the d-orbitals are empty, from carbon-metal bonding orbitals into d-orbitals. Either should weaken the metal-carbon bond. It appears that for the formation of a stable organometallic compound it is essential to have more than a certain minimum energy difference between the highest energy orbital which contains electrons and the lowest energy orbital which is vacant. In most transition metal compounds, with their rather close d energy levels, this minimum is not attained. The special instability thereby conferred on the metal-carbon bond may perhaps be related to the formation of an unstable entity (radical or carbanion) on fission of this bond, whereas a comparable instability would not characterize a metal-amine or metal-halogen bond since its rupture would give ions, atoms, or molecules that could recombine with the metal ion . This is consistent with the special position occupied by chromium(III). Chromium(III) complexes have three unpaired electrons, each in a non-bonding d orbital. There is little tendency for these electrons to be promoted to anti-bonding orbitals because of lack of help by interelectronic repulsions. On the other hand, promotion from bonding orbitals into these will be hindered by the energy needed to pair the promoted electron with the one already in the non-bonding orbital.

The premise that a change in energy larger than some crucial value is essential for stability has been supported by results obtained for alkyl and aryl complexes of Group VIII elements stabilized by tertiary phosphines. Complexes studied were those where the d orbitals not used in sigma bonding are at least singly occupied by electrons.

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REACTION OF PEROXYMONOSULFURIC ACID WITH HYDROGEN PEROXIDE IN THE PRESENCE OF MANGANOUS AND CUPRIC CATIONS

R. Ferrús March 1, 1960

INTRODUCTION

The reaction $$H_2SO_5 + H_2O_2 \xrightarrow{MnSO_4} H_2SO_4 + H_2O + O_2 \qquad (I)$$

was reported a long time ago, but the only experimental support found in the literature is based on the fact that when hydrogen peroxide solutions containing peroxymonosulfuric acid are titrated with a standard potassium permanganate solution, the values obtained for hydrogen peroxide concentrations are low because of a loss of active oxygen (1). The observation by Baeyer and Villiger (2) concerning the ability of peroxymonosulfuric acid to oxidize Mn(II) to Mn(III), together with the fast reaction of Mn(III) with H_2O_2 (3), lead to the assumption that the Mn(II) which appears during the oxidation of H_2O_2 by $KMnO_4$, acts as a catalyst according to equation (I). Thus a loss of active oxygen occurs. This explanation is no longer a satisfactory one because the reaction of H_2SO_5 with Mn(II) is very slow in presence of H_2O_2.

Besides the catalytic action of Mn(II), Price (1) admitted the possibility of a reaction between H_2O_2 and H_2SO_5 induced by the oxidation of H_2O_2 by permanganate. The chemical induction is now perfectly understood in terms of formation of active intermediates (4). The explanation based on chemical induction seems to be the correct one for the interference of peroxymonosulfuric acid in the titration of H_2O_2 with permanganate or, more generally, with any standard oxidant solution.

II. ANALYTICAL METHOD AND STOICHIOMETRY

In order to establish a rate law, we must follow the concentration changes of hydrogen peroxide and peroxymonosulfuric acid with time. The determination of individual peroxycompound concentrations in a solution containing hydrogen peroxide, peroxymonosulfuric acid, and peroxydisulfuric acid has received repeated attention (5). Although there is no peroxydisulfuric acid in our system, this does not improve the situation very much because most of the trouble comes from the mutual presence of H_2O_2 and H_2SO_5. Every analytical procedure found in the literature was either considered or tested for our solutions, and none was found suitable. Finally a method was adopted consisting in a determination of the total oxidant present in the solution. From this value and the stoichiometry of the reaction the molar concentrations of $[H_2SO_5]$ and $[H_2O_2]$ were calculated. The stoichiometric ratio was found to be 1:1.

III. REACTION KINETICS

No reaction was observed between H_2SO_5 and H_2O_2 without catalyst; or if there is any reaction, it is so slow that it cannot interfere with the catalyzed one.

The total order of reaction, as determined in solutions in which both reactants have the same concentration, is 2.

To find out the order with respect to each reactant (6), solutions containing a different initial concentration for each peroxy-compound were studied. In those solutions with a larger proportion of H_2O_2 the rate law is

$$\frac{d\,[H_2SO_5]}{dt} = \frac{d\,[H_2O_2]}{dt} = -k\,[H_2O_2][H_2SO_5] \qquad (II)$$

When the H_2SO_5 concentration is larger than that of H_2O_2, the rate law is

$$\frac{d\,[H_2SO_5]}{dt} = \frac{d\,[H_2O_2]}{dt} = -k\,[H_2SO_5]^2 \qquad (III)$$

IV. CUPRIC SULFATE AS A PROMOTER IN THE MANGANOUS SULFATE CATALYSIS

Bohnson and Robertson (7) have shown that the rate of evolution of oxygen in the catalytic decomposition of hydrogen peroxide by a mixture of iron and copper salts is much more rapid than the rate which may be calculated on the assumption that each salt acts independently. This phenomenon is quite frequent in heterogeneous catalysis and is known as "promoter action", but cases of promotion in homogeneous catalysis are not numerous. The copper salts alone are very poor catalysts in the decomposition of H_2O_2, but when added to a system containing iron salts the catalytic activity of these is highly increased. The effect of copper salts increases rapidly with the concentration of promoter until a limit is reached, so that further addition does not increase the rate of decomposition of H_2O_2.

The same results were obtained when small amounts of cupric sulfate were added in our solutions, and no reaction was observed with cupric sulfate alone.

This promoter action has been explained by Barb _et. al._ (8) in terms of entropies of activation within the transition state theory.

V. AN UNEXPECTED VARIABLE: THE DIFFERENCE BETWEEN INITIAL CONCENTRATIONS OF REACTANTS.

Inasmuch as the stoichiometry of reaction (I) is 1:1, the difference between the initial concentrations of peroxymonosulfuric acid and hydrogen peroxide remains constant through the reaction. When this difference is changed from one solution to another, the rate constant obtained from the new solution does not have the same value. The maximum value for k corresponds to those solutions in which the concentration for both reactants is identical, and k decreases as the difference increases. This could be expressed by some equation like

$$k = k_0 - k_1 \quad ([H_2SO_5] - [H_2O_2])^2 \qquad \text{(IV)}$$

although a larger number of experimental results would be necessary to check (IV) quantitatively.

VI. MANGANOUS SULFATE CONCENTRATION, ACIDITY, AND IONIC STRENGTH

Information about the influence of these variables on the reaction rate was obtained by running several series of experiments, each two series being different only in one variable. In every series, a plot of k vs. cupric sulfate concentration was made, and from comparison between pairs of curves the influence of the variable modified was considered.

The reaction is first order with respect to manganous sulfate.

The hydrogen ion concentration has very small influence. Only a slight increase in rate was observed when $[H^+]$ was changed from 0.100 to 0.050.

More important is the ionic strength. The rate constant increases about 30% of its value when varies from 0.16 to 0.09.

VII. PROPOSING A MECHANISM

Several possibilities of chain mechanisms can be discussed in order to explain different kinetic aspects of the system, but unfortunately it has not been possible to propose a single mechanism which accounts for all the experimental results observed.

This research was done in the Facultad de Ciencias, Universidad de Valencia under the direction of Dr. Beltrán Martinez, Professor of Inorganic Chemistry at that University. Economic support from the Diputacion Provincial de Valencia and the Comisaria de Proteccion Escolar is gratefully acknowledged.

[illegible]

[illegible] CONDUCTIVITY [illegible] (CONTINUED).

[illegible]

although a [illegible] number of experimental results would be necessary to check [illegible] quantitatively.

VI. [illegible] ELECTRIC CONDUCTIVITY, [illegible]

[illegible]

The reaction is first order with respect to [illegible].

[illegible]

[illegible]

VII. [illegible] MECHANISMS

Several possibilities [illegible] mechanisms [illegible] be discussed in order to explain different kinetic aspects of the system, but unfortunately it has not been possible to propose a [illegible] which accounts for all the experimental results obtained.

This research was done in the Facultad de Ciencias, Universidad de Valencia, under the direction of Dr. [illegible], Professor of Inorganic Chemistry at that University. Economic support from the Diputación Provincial de Valencia and the [illegible] is gratefully acknowledged.

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REACTIONS OF ELEMENTAL PHOSPHORUS. I.

Jerome Wuller March 8, 1960

I. INTRODUCTION

Elemental phosphorus reacts with most metals, with all non-metals except the inert gases, and with many organic and inorganic compounds. This seminar will deal with the reactions of elemental phosphorus with inorganic nonmetallic substances, excepting the halogens.

II. ELEMENTAL PHOSPHORUS

Elemental phosphorus exists in several allotropic forms. White phosphorus, which is composed of P_4 tetrahedra, is the most reactive (1-3). Oxidation potentials characteristic of the element and its compounds are as follows (4):

$$PH_3 \xrightarrow{(0.0)} P_2H_4 \xrightarrow{(0.1)} P \xrightarrow{0.51} H_3PO_2 \xrightarrow{0.50} H_3PO_3 \xrightarrow{0.28} H_3PO_4$$

$$PH_3 \xrightarrow{(0.8)} P_2H_4 \xrightarrow{(0.9)} P \xrightarrow{2.05} H_2PO_2 \xrightarrow{1.57} HPO_3 \xrightarrow{1.12} PO_4$$

III. BONDING IN PHOSPHORUS COMPOUNDS

The directional characteristics observed in chemical compounds of phosphorus may be approximated by those of five sets of sigma orbitals: *p*, *sp*^{3}, *p*^{3} with some *sp*^{3} character, *sp*^{3}*d*, and *sp*^{3}*d*^{2} (1). About 200 kcal. are needed to promote a 3*p* electron into a 3*d* orbital; so *sp*^{3}*d* and *sp*^{3}*d*^{2} hybrids are rare. About 700 kcal. are needed to ionize phosphorus to the + state. Hence compounds of phosphorus and non-metals are covalent.

PXYZ compounds have bond angles between 90° and 109°28'. (Simple relationships between bond angles and molecular properties should not be expected.) Exceptions are P_4 and P_4S_3: they apparently have "bent *p* bonds". Stability of the P_4 molecule is enhanced by "pseudo-chelate" bonding.

PWXYZ compounds may be thought of as Lewis acid-base complexes in which *d* bonds are used to give pi bonding. Examples are POF_3 and H_3PO_2.

Five- and six-coordinate phosphorus compounds are rare. They have less than one sigma bond per ligand and little pi bonding.

IV: OXIDATION

The most important reaction of elemental phosphorus is oxidation. Study of the phenomena involved led to the development of the theory of branching chain reactions by Nobel Laureate Semenoff (5). There are upper and lower critical pressures of oxygen for a given pressure of phosphorus. Between these critical pressures, ignition of the

phosphorus vapor occurs; outside of this range of oxygen pressures, the rate of oxidation is very slow. The critical pressures are practically independent of temperature, but are affected by the addition of other gases. The lower critical pressure is inversely proportional to the square of the diameter of the containing vessel and to the pressure of phosphorus vapor. The upper critical pressure is independent of the diameter of the container and directly proportional to the pressure of phosphorus vapor (6).

The following sequence of reactions is consistent with the above data (7):

$$P_4 + O_2 \rightarrow P_4O + O$$
$$P_4 + O + M \rightarrow P_4O + M$$
$$P_4O_n + O_2 \rightarrow P_4O_{n+1} + O \quad (n = 1, 2....9)$$
$$O + O_2 + M \rightarrow O_3 + M$$
$$O + X \rightarrow \text{stable product}$$
$$O + \text{wall} \rightarrow \text{adsorbed oxygen}$$

The main product is P_4O_{10}.

The oxides P_4O_6 and PO_2 (8) have been prepared and studied. Amorphous P_xO structures, which often contain hydrogen, have been reported in the literature, e.g. $P_{4_n}O_nH_n$ (9).

Red phosphorus suspended in sodium hydroxide solution reacts with hypohalogenites to give sodium hypophosphate (10). Another product of this complex reaction is $(NaPO_2)_6$, the salt of a new cyclic acid (11).

V. REACTIONS WITH SULFUR

"The history of the compounds of phosphorus and sulfur is truly a comedy of errors. Compounds diligently investigated and carefully described by one worker could not be prepared by another worker or else are represented as mixtures."

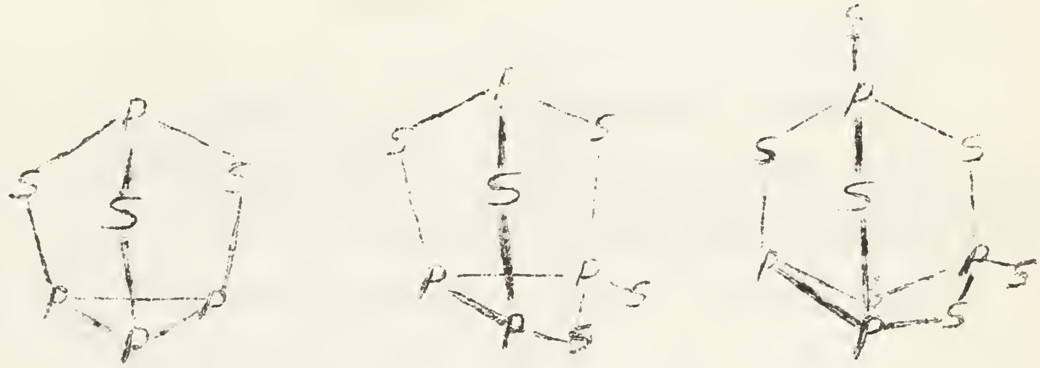
--B. Herscovici

The sulfides P_4S_3, P_4S_7, and P_4S_{10} can be prepared by thermal reaction between phosphorus and sulfur (12-19). The compounds $P_4S_3O_4$ (19) and $P_4S_3I_2$ (20) can be prepared by oxidation and iodination of P_4S_3 in carbon disulfide. The compound P_4S_5 has been prepared by slow cooling of molten mixtures of phosphorus sulfides (21) and by treatment of P_4S_3 with sulfur and iodine in carbon disulfide (22). Iodine also catalyzes the reaction of elemental phosphorus with an excess of sulfur (16). If this reaction is carried out in xylene, the slightly soluble intermediate P_4S_7 accumulates (21). The main product on long refluxing of the mixture is P_4S_{10}.

A possible mechanism for this reaction involves simultaneous coordination of iodine and a sulfur atom or chain to adjacent phosphorus atoms, followed by molecular rearrangement to give the P-S-P structure.

Three such steps may produce P_4S_3. The compound P_4S_3 reacts rapidly with sulfur to give P_4S_7 (21). Slow reaction of sulfur with P_4S_7 gives P_4S_{10}.

Structures of P_4S_3 (23, 24) P_4S_5 (25), and P_4S_7 (26, 27) are as follows:



VI. REACTIONS WITH SELENIUM AND TELLURIUM

Selenides with the empirical formulas P_2Se_3 and P_2Se_5 have been prepared by direct reaction of the elements (28-30). The compound P_2Te_3 also has been prepared (31). The compounds $P_4Se_3I_2$ (29) and $P_4Te_3I_2$ (31) have been obtained by reaction of P_4Se_3 and P_4Te_3 with iodine in carbon disulfide.

VII. REACTIONS WITH NITROGEN

The diatomic molecule PN is unstable at room temperature (1). The solid phosphorus nitrides produced by use of electrical discharges are amorphous to X-rays and usually appear to be heterogenous. A crystalline phosphorus nitride has been prepared (32). This compound has the empirical formula P_3N_5 (33).

Treatment of amorphous nitrides produced by arc discharges with ammonia or nitrogen at high temperatures yielded crystalline residues with the same X-ray pattern as P_3N_5. Similar treatment of homogenous amorphous nitrides produced by thermal methods yielded small amounts of the same crystal phase (33).

VIII. DISPROPORTIONATION REACTIONS

Disproportionation reactions are described by the equations

$$P_4 + 6H_2O \xrightarrow[\text{heat or catalysts}]{} 2\ PH_3 + 2\ H_3PO_3$$

$$2\ PH_3 + 8\ H_2O \xrightarrow[\text{(slow)}]{} 2\ H_3PO_4 + 8\ H_2$$

$$2\ H_3PO_3 + 2\ H_2O \xrightarrow[\text{(slow)}]{} 2\ H_3PO_4 + 2\ H_2$$

$$P_4 + 3\ OH^- + 3\ H_2O \longrightarrow PH_3 + 3\ H_2PO_2^-$$

One possible mechanism for the alkaline disproportionation of phosphorus involves successive nucleophilic attack on the phosphorus molecule by hydroxide ions, causing P-P bond rupture followed by proton transfer from the solvent (34).

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REACTIONS OF ELEMENTAL PHOSPHORUS. II.

Jerome Wuller March 15, 1960

I. INTRODUCTION

Preparations, structures and properties of the phosphorus hydrides and halides and the metal phosphides are interesting and often unusual.

II. PHOSPHORUS HYDRIDES

Spectra of mixtures of phosphorus vapor and hydrogen show the presence of a molecule, PH, which does not exist at room temperature. Phosphine, PH_3, is a product of the reaction of atomic hydrogen with phosphorus (1). Mixtures of phosphine, biphosphine, and hydrogen are produced by disproportionation of phosphorus and by hydrolysis of metal phosphides (2,3). Pure phosphine may be obtained by treatment of phosphonium iodide with bases (4).

Phosphine is formed slowly on heating phosphorus in hydrogen at high temperatures and pressures. The equilibrium constant for the reaction $P_4(g) + 6\ H_2 \rightleftarrows 4\ PH_3$ is about 10^{-12} atm.$^{-3}$ at 600° and about 10^{-13} atm.$^{-3}$ at 1000°. The enthalpy change for this reaction is about -23 kcal. (5). Although phosphine is thermodynamically unstable with respect to its elements, it decomposes immeasurably slowly at room temperature (2).

The observed dipole moment of phosphine, 0.55 D, cannot be explained on the assumption of pure covalent bonding with pure p-orbitals for the phosphorus atom. Approximate calculations indicate that the experimental value can be explained on the assumption of several percent of s-hybridization (6).

Biphosphine, P_2H_4, is generally obtained as a byproduct in the manufacture of phosphine. Though it is fairly stable at -80°, it disproportionates rapidly into phosphine and lower phosphorus hydrides at 0°. It can explode violently under the influence of heat, light, or traces of catalysts (2,3).

Solid yellow $(PH)_n$ compounds have been prepared in excellent yields by reactions of phosphorus trihalides with metallic hydrides. Temperatures around 0° gave best yields. The mechanism of reaction may involve formation of the unstable intermediate PH_2Br, followed by intermolecular dehydrohalogenation to give a chain polymer similar to $(-SiH_2-)_n$ or S_x (7).

Amorphous yellow phosphorus hydrided with empirical formulas $P_{\geq 2n}H_n$ are produced by the decomposition of phosphine, by the hydrolysis of P_2I_4, and by treatment of metal phosphides with dry HCl or water (8). Disproportionation of white phosphorus with potassium hydroxide in glycerin also gives such a hydride (9). Heating these yellow phosphorus hydrides in vacuum produces phosphine, some hydrogen, and orange or reddish compounds (10). It has been postulated that these compounds are mixtures of red phosphorus and adsorbed phosphine (11). Biphosphine decomposes in a sealed system to give the yellow solid hydride $P_{2.25n}H_n$. Decomposition of this hydride under controlled conditions produces nonstoichiometric solid hydrides of practically any composition above that P:H ratio (12).

The general concept of a polymer system composed of $-PH_2$ terminal units, -PH- chain units, and -P- branching units has been set forth by van Wazer (3). For hydrides in which the P:H atomic ratio is more than unity, branching must be present. The higher the P:H ratio, the more branching must be present. The limiting case is an amorphous three-dimensional "red phosphorus" polymer.

The unknown molecule PH_5 should be thermodynamically unstable.

III. PHOSPHORUS HALIDES

The molecules PCl, PBr, and PI are unstable under normal conditions but they have been studied by spectroscopic methods.

Reactions of red or white phosphorus with the halogens yield mixtures of PX_3, PX_5, and P_2X_4 molecules (13-16). Phosphorus trifluoride is usually prepared by halide exchange (17). Mixed trihalides are prepared by heating mixtures of trihalides or by halogen exchange (18,19). Rates of exchange in the systems $POCl_3$-$POBr_3$ and $PSCl_3$-$PSBr_3$ are much slower than those of the trihalide systems (20).

The molecule PF_5 is stable. The molecules PCl_5 and PBr_5 exist in equilibrium with the trihalides and halogens in the gas phase: the pentachloride is more stable than the pentabromide. The molecule PI_5 is unknown. The decreasing stability observed in this series is due to a combination of steric and electronic effects.

In the solid state, and also in solvents of high dielectric constant, PCl_5 and PBr_5 form ions in accordance with the formulas PCl_4^+ PCl_6^- and PBr_4^+ Br^-. In carbon tetrachloride, three-fifths of the chlorine atoms of PCl_5 exchange rapidly with those of elemental chlorine but two-fifths exchange very slowly (21). In acetonitrile, the PCl_6^- ion exchanges rapidly with chloride ion but the PCl_4^+ ion exchanges slowly (22).

The compound P_2I_4 can be prepared by reaction of white phosphorus with stoichiometric amounts of iodine in carbon disulfide (23-25). Treatment of a mixture of P_4 and P_2I_4 with water in carbon disulfide yields PH_4I (26). The compounds $(CF_3)_3P$, $(CF_3)_2PI$, and $(CF_3)PI_2$ can be prepared by the reaction of white or red phosphorus with trifluoroiodomethane and iodine in a bomb (27).

Mixtures of phosphorus and bromine are used to prepare alkyl bromides from alcohols (28) and to brominate organic acids (29). Mixtures of red phosphorus and iodine or hydriodic acid are used to reduce various organic compounds (30).

IV. PHOSPHIDES

Most metallic elements form several phosphides, each a stoichiometric compound. Some metal phosphides have formulas which correspond to classical valency rules, but this is far from common. An excellent review of the field has been presented by van Wazer (3).

Phosphides have been prepared by the direct combination of metal and phosphorus under various conditions; by the reaction of phosphine or phosphorus trichloride with a metal or a compound of a metal; by the reaction of phosphorus with a compound of a metal; by the reduction of a mixture of a metal or metal compound and a phosphate or phosphite; by the thermal decomposition of a metallic phosphate or phosphite; by the reaction of a phosphide with a metal or the thermal decomposition of one phosphide to another; and by fused salt electrolysis (31).

The preparation of transition metal phosphides by fused salt electrolysis has been investigated recently by Yocom (31). Electrolysis of sodium metaphosphate at 850-900° produces phosphorus at the cathode. When a molten lead cathode was used, no sodium could be detected (by radiotracer methods) in the lead after electrolysis. This indicates that elemental sodium is not an intermediate in the reduction. Trisodium orthophosphate is the other product of reduction. Carbon monoxide, carbon dioxide, and "NaP_3O_8" glass are the products of oxidation at a carbon anode.

Potential measurements with metaphosphate (meta) and pyrophosphate (pyro) melts containing iron, cobalt, or nickel show fundamental differences in the formation of phosphide. Meta melts show a potential corresponding to the pure meta decomposition potential and produce crystalline phosphides. With a pyro melt, the metal is produced; and after the electrode is polarized with respect to the metal, phosphorus is produced. The combination of the metal and phosphorus results in the production of phosphides as black powders or in the crystal form of the metal.

Vanadium, chromium, and manganese phosphides could not be produced from meta melts, but they could be obtained from mixed pyro-ortho melts. Titanium phosphide could not be produced from meta or pyro melts.

Apparently the decomposition potential of meta is less than pyro, and that of pyro is less than that of orthophosphate melts. Apparently the phosphides are produced by more or less simultaneous deposition of metal and phosphorus. Hence differences in production of transition metal phosphides by fused salt electrolysis can be explained by differences in thermodynamic equilibrium cell potentials (31).

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LIQUID ANHYDROUS HYDROGEN FLUORIDE AS AN NON-AQUEOUS SOLVENT

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Argonne National Laboratory

March 29, 1960

I. PHYSICAL PROPERTIES OF HYDROGEN FLUORIDE
   A. Comparison with water
   B. Polarity and electrical conductance
   C. Anomolous viscosity and surface tension
   D. Hydrogen bonding in liquid hydrogen fluoride

II. HYDROGEN FLUORIDE AS A SUPER ACID
   A. The Hammett acidity function
   B. -HO values for HF
   C. Comparison of the acid properties of HF to other strong acids.

III. ACIDS IN THE HYDROGEN FLUORIDE SYSTEM
   A. Acid-base equilibria in HF
   B. Infrared studies in the $HF-SbF_5$ system
   C. Equilibria in the $HF-SbF_5$ and $HF-NbF_5$ systems
   D. Raman spectrum of $HF-SbF_5$ system

IV. EXPERIMENTAL TECHNIQUES IN HYDROGEN FLUORIDE STUDIES
   A. Vacuum line manipulation
   B. Spectrophotometric equipment
   C. Infrared cells
   D. Raman cells
   E. Electrical conductivity cells

V. SOLUTES IN HYDROGEN FLUORIDE
   A. Simple organic molecules as studied by infrared spectroscopy
   B. Protein behavior in HF

VI. HYDROGEN FLUORIDE SOLVENT SYSTEMS
   A. The $HF-SO_2$ system
   B. The $HF-CO_2$ system

SPINELS

Robert C. Fay

April 5, 1960
April 7, 1960

Metal oxides having the spinel structure are of interest from both a practical and a theoretical point of view. They are of technological importance because of their unusual electrical and magnetic properties. They are of theoretical interest because they provide a test for theories of magnetic exchange interaction and for the crystal field theory.

I. CRYSTAL STRUCTURE

The spinel crystal structure (1-11) may be described as an approximately face-centered cubic array of oxide ions in which some of the octahedral and tetrahedral interstices are occupied by metal cations. The unit-cell formula for a normal 2-3 spinel is $X_8Y_{16}O_{32}$, where X is a divalent cation and Y is a trivalent cation. In the normal spinels, the divalent ions occupy the tetrahedral sites, and the trivalent cations occupy the octahedral sites. In the inverse spinels (12), $Y_8[X_8Y_8]O_{32}$, the tetrahedral sites are occupied by the trivalent cations, and the octahedral sites are equally populated by divalent and trivalent cations.

The oxygen parameter $\underline{u}$ is defined as the perpendicular distance in units of $\underline{a}$ from the face of the unit cell to the oxide ion, which in an ideal face-centered cubic oxide array has a coordinate 0.375 $\underline{a}$. The parameter, $\underline{a}$, is the length of the unit cell. If the oxygen parameter is greater than 0.375, the tetrahedral site is expanded relative to the ideal spinel. In all known spinels the oxygen parameter is greater than 0.375.

II. TYPES OF SPINELS

In addition to normal and inverse spinels, mixed spinels are well known. The mixed spinels are characterized by the presence of divalent and trivalent cations in both the octahedral and the tetrahedral sites. The distribution of cations between the octahedral and tetrahedral sites has been found to be temperature dependent (10,13-16). The cation distribution obeys the Boltzmann distribution law.

Although the 2-3 spinels are the most common valency type, other types (eg. 4-2) have been described (6,8,11,17-21). All kinds of metal ions except the lanthanides and the actinides have been found in spinel type oxides. Mixed spinels of various valency types have been described (21-27).

The γ - trivalent oxides of iron, aluminum, chromium, and manganese have a defect spinel structure with the cation vacancies found in the octahedral sites (8,28-32). γ - Fe_2O_3 has been found to contain small amounts of water, which has suggested that some of

the oxide ions are replaced by hydroxide ions (30,31). Thio- and selenospinels have also been described (33-36). These compounds are completely analogous to the oxygen-containing spinels.

III. PREPARATION AND ANALYSIS

The oxygen-containing spinels are usually prepared by heating a stoichiometric mixture of the appropriate oxides at temperatures ranging from 800°C. to 1400°C. (4,12,37-39). Alternatively, they may be prepared from the metal carbonates (2). The thiospinels may be prepared by heating a stoichiometric mixture of the sulfides in vacuo at 900°C. or by heating the metals in a stream of anhydrous hydrogen sulfide at 1000-1100°C. (34,35). The resulting compounds may be identified and analyzed by x-ray diffraction and spectrochemical methods and by classical chemical techniques (22,38-39).

IV. EXPERIMENTAL METHODS FOR STRUCTURAL INVESTIGATION

The distribution of cations between the octahedral and tetrahedral sites has been studied by x-ray diffraction, neutron diffraction, saturation magnetization measurements, and to a far lesser extent by infrared spectroscopy and paramagnetic susceptibility measurements. The x-ray method has been applied extensively (4,6,12,13,17,25,27-32,34,37,41), but it is limited by the similarity in scattering power of atoms having nearly the same atomic number. Neutron diffraction has been employed in determining the magnetic structure as well as the chemical structure of transition-metal spinels (2,5,23,24,42-47).

The ferrimagnetic spinels exhibit a transition temperature called the Curie temperature. Above the Curie temperature, the spinels are paramagnetic. Below the Curie temperature, the electronic magnetic moments at the octahedral and tetrahedral sites are aligned antiparallel. The net magnetic moment when extrapolated to 0°K. is called the saturation magnetization. Thus the saturation magnetization of $Fe^{III}[Fe^{II}Fe^{III}]O_4$ should be and is $(4 + 5)-(5) = 4$ in units of unpaired electrons. (Ions enclosed in brackets are in the octahedral sites). The saturation magnetization of $MgFe_2O_4$ is 1.1. The cation distribution may be calculated by assuming the formula $Mg_xFe_{1-x}[Mg_{1-x}Fe_{1+x}]O_4$. We obtain the linear equation

$$[5(1 + x) + 0(1 - X)] - [5(1 - X) + 0(X) = 1.1$$

which yields X = 0.11. By similar methods, the cation distribution in a rather large number of spinels has been deduced (14,18,21,22, 52,53). The theory of antiferromagnetic coupling of metal ions through the intermediate oxide ion (super exchange theory) was first applied to the spinels by Néel (48). Several excellent reviews of the super exchange theory have appeared recently (10,49-51). The simple Néel theory does not apply to all spinels (54). The temperature dependence of magnetic moments below the Curie temperature has been studied by Pauthenet (55). Paramagnetic susceptibility measurements have been utilized by Cossee (56,57) to determine the cation distribution in Co_3O_4.

Attempts have been made to relate force constants obtained by infrared spectroscopy to cation distributions and covalent bond strengths (58,59). No definitive conclusions can be made as yet.

V. EXPERIMENTAL CATION DISTRIBUTIONS

The known cation distributions of the most common 2-3 spinels are presented in Table 1. Cation distribution is indicated as normal (N) or inverse (I), followed by the method of determination and the reference. The numerical values included indicate the energy preference for the normal structure over the inverse structure as predicted by crystal field theory.

VI. FACTORS WHICH DETERMINE THE CATION DISTRIBUTION

Since the trivalent ions are smaller than the divalent ions and since the tetrahedral sites are smaller than the octahedral sites the inverse arrangement would be expected. However, calculations based on an electrostatic model favor the normal arrangement for values of $\underline{u}$ greater than 0.379 and favor the inverse structure for values of $\underline{u}$ less than 0.379 (6,61).

The effect of electronic configuration on cation distribution has been treated by the valence bond approach (3,6) and by crystal field theory (60,62). The valence bond approach leads to the following rules:

1. Ions with electronic configuration d^5(Mn^{2+}, Fe^{3+}) and d^{10}(Zn^{2+}, Cd^{2+}) prefer tetrahedral sites because of a tendency to form sp^3 tetrahedral covalent bonds.
2. Ions with configuration d^4(Mn^{3+}) and d^9(Cu^{++}) prefer octahedral sites because of a tendency toward dsp^2 square coplanar covalent bonds.
3. Ions with configuration d^3(Cr^{3+}) and d^6(Co^{3+}) prefer octahedral sites because of a tendency to form d^2sp^3 octahedral covalent bonds.

Crystal field theory allows calculation of a crystal field stabilization energy (CFSE) based on known electronic configurations and energy parameters (Dq) obtained from visible spectra. For each transition metal ion, an octahedral site preference energy (OSPE) may be defined. The OSPE is the difference between the CFSE in the octahedral site and the CFSE in the tetrahedral site. The cation distributions predicted by the OSPE are seen to be in error only for the aluminates. Miller (63) has recently derived an OSPE for transition metals and non-transition metals by taking into account coulomb energy, Born repulsion energy, and CFSE.

VI. TETRAGONAL DISTORTIONS

The c/a ratios of known tetragonal spinels are presented in Table 2.

Table 1. Experimental Cation Distributions in 2-3 Spinels.

X^{2} \ Y^{3+}	Al^{3+}	Ga^{3+}	Fe^{3+}	Cr^{3+}	Mn^{3+}	V^{3+}	Co^{3+}
Mg^{2+}	N, neutron (43) 0	I, x-ray (12) 0	0.89I, sat. mag. (22) 0.88I, neutron (2) 0.9I, neutron (23) I, x-ray (12) 0	N, x-ray (6) N, x-ray (37) +37.7		N, x-ray (37) N, x-ray (41) +12.8	
Zn^{2+}	N, x-ray (12) 0		N, neutron (5) N, x-ray (6) 0	N, x-ray (37) +37.7	N, (60) +22.8	N, x-ray (37) N, x-ray (41) +12.8	N, paramag. sus. (57) +19
Cd^{2+}	N, x-ray (6) 0	N, x-ray (37) 0	N, x-ray (6) 0	N, x-ray (6) +37.7			
Mn^{2+}	0.66N, x-ray (4) N, x-ray (12) 0		0.81N, neutron (44) 0	N, x-ray (6) +37.7	N, para-mag. sus. (29) +22.8	N, x-ray (41) +12.8	
Fe^{2+}	N, x-ray (12) -4.0		I, sat. mag. (22) I, neutron (42) -4.0	N, x-ray (6) +33.7		N, x-ray (41) +8.8	
Co^{2+}	0.81N, x-ray (4) N, x-ray (12) -7.4		I, sat. mag. (22) I, neutron (46) -7.4	N, x-ray (6) +30.3			N, paramag. sus. (57) +11.6
Ni^{2+}	0.85I, x-ray (4) -20.6	I, x-ray (4) -20.6	I, sat. mag. (22) I, neutron (5) -20.6	N, x-ray (6) +17.1			

Table 1 (Continued)

X^{2} \ Y^{3+}	Al^{3+}	Ga^{3+}	Fe^{3+}	Cr^{3+}	Mn^{3+}	V^{3+}	Co^{3+}
Cu^{2+}	0.56N, x-ray -15.2		I, x-ray (6) 0.96I, sat.mag. (22) I, neutron (45) -15.2	N, x-ray (25) N, neutron (47) +22.5			

Table 2. c/a Ratios of Tetragonal Spinels.

Spinel	c/a at 25°C.	Reference
Mn_3O_4	1.16	29,66
$-Mn_2O_3$	1.16	29
$ZnMn_2O_4$	1.14	3
$CuFe_2O_4$	1.06	45
$CuCr_2O_4$	0.91	27,46
	1.04(-170°C.)	
$NiCr_2O_4$	1.022(27°C.)	66
	1.00(34°C.)	
$CuRh_2O_4$	0.91	65
$NiRh_2O_4$	1.038	65
$CuAl_2O_4$	1.00	25

Verwey et al. (64) have attributed tetragonal distortions to cation ordering in the octahedral sites. Goodenough and Loeb (3) have explained distortions in copper and manganese spinels on the basis of dsp^2 covalent bonds in the octahedral sites. Dunitz and Orgel (1) and McClure (60) have accounted for tetragonal phases in terms of the Jahn-Teller effect. The c/a ratio has been found to decrease upon substitution of an ion which has no orbital degeneracy for an ion which has orbital degeneracy (25-27). A theoretical model for cubic to tetragonal phase transformations has been set up by Wojtowicz (66,67). Miller (68) has employed the theory of cooperative distortions to demonstrate the presence of Mn^{3+} and Fe^{2+} rather than Mn^{2+} and Fe^{3+} when manganese and iron coexist in octahedral sites. $-Mn_2O_3$ shows tetragonal distortion at both the octahedral and the tetrahedral sites. Sinha and Sinha (29) have accounted for the distortion in the tetrahedral sites on the basis of d^2sp irregular tetrahedral bonds. Sinha (69) has implied that a strong field in the tetrahedral site must be assumed in order to explain the paramagnetism of γ-Mn_2O_3 in terms of crystal field theory.

VII. ELECTRICAL CONDUCTIVITY

Electrical conductivity in the spinels is due to the presence of a metal in two different oxidation states on equivalent crystallographic sites (7,70,71). The sudden decrease in the electrical conductivity of Fe_3O_4 at 120°K. has been attributed to an ordering of the Fe^{2+} and Fe^{3+} ions in the octahedral sites (70). Semiconductivity in the system $Co_{3-x}Fe_xO_4$ has been observed by Jonker (72).

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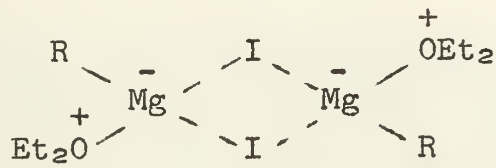
REACTIONS OF GRIGNARD REAGENTS WITH TRANSITION METAL HALIDES

George L. Morgan April 26, 1960

I. NATURE OF GRIGNARD REAGENTS

Alth gh Grignard reagents have been known for some time, the exact nature of their structure has not yet been established (1). A probable structure might be



for an unionized species. Some interesting work has been done on the electrolysis of Grignard reagents in diethyl ether (2). The main course of the reaction is the liberation of organic free radicals at the anode, which then disproportionate or couple. Straight chain hydrocarbon radicals (C = 4 or more) and substituted n-propyl free radicals were observed to couple completely.

II. REACTIONS OF GRIGNARD REAGENTS IN THE PRESENCE OF TRANSITION METAL HALIDES

Kharasch and Tawney (3) became interested in the changes in the course of some reactions caused by the presence of transition metal salts. Their work on the reaction of isophorone with MeMgBr led Kharasch and coworkers to study additonal systems (4,5,6).

To further an understanding of the reaction, Kharasch and Fields (7) noted that:

1.) Arylmagnesium halides do not react with monosubstituted aryl halides.

2.) Metal halides do not react with aryl halides.

3.) Arylmagnesium halides react with transition metal halides to yield bi-aryl compounds:

$$2RMg + MX_2 \rightarrow R - R + 2MgX_2 + M.$$

However, when one made of ϕBr is added to one equivalent of ϕMgBr, with only a trace (3%) of cobaltous chloride present, a vigorous reaction ensues. Phenylbromide is the oxidizing agent and does not take part in the direct formation of biphenyl. Kharasch then proposed this mechanism:

$$\phi MgBr + CoCl_2 \rightarrow \phi CoCl + MgBrCl$$
$$2\phi CoCl \rightarrow \phi - \phi + 2CoCl\cdot$$
$$CoCl\cdot + \phi Br \rightarrow CoClBr + \phi\cdot$$
$\phi\cdot \rightarrow$ benzene, trace biphenyl, and other polymers.

Wilds and McCormack (8) pointed out that all work (of Kharasch and others) indicates that RCoCl and CoCl· are unstable. Further, there was no experimental evidence for CoCl·. They further observed that the reaction of the Grignard reagent with $CoCl_2$ can be carried out hours before the addition of the organic halide. Some catalytic activity was even retained for weeks. They proposed a mechanism whereby the active species is colloidal pyrophoric cobalt. Gilman, Jones, and Woods (9,10) also favored the formation of free metal to explain the coupling products obtained when copper, silver, and gold salts were reacted with methyl lithium.

Smith (11), in order to test the free cobalt mechanism, prepared active cobalt and attempted to react it with ethyl bromide. No evolution of any gaseous products was observed. Smith (12) further carried out radiotracer studies which argue for the Kharasch type mechanism.

Kharasch and co-workers (13) have expanded their theory by explaining the free radical formation as a function of the reducing powers of the organic anions. They have hopes of thereby establishing a series of relative reducing powers.

III. ORGANO-TRANSITION METAL COMPOUNDS

In 1955, Cotton (14) reviewed this subject, which then consisted of experimental attempts to make stable σ-bonded compounds. Gilman and Lichenwalter (15) suggested that the rate of coupling would be a fair measure of the stabilities. In their study of the reaction of ØMgBr with metal halides, they observed that iron, cobalt, nickel, ruthenium, rhenium, and palladium halides gave almost quantitative yields of biphenyl, whereas osmium, iridium, platinum, and copper halides were significantly lower. Jaffé (16) made some approximate calculations based on Mulliken's "Magic Formula", which showed why the transition metals would have weaker bonds and why copper compounds should have a particular stability.

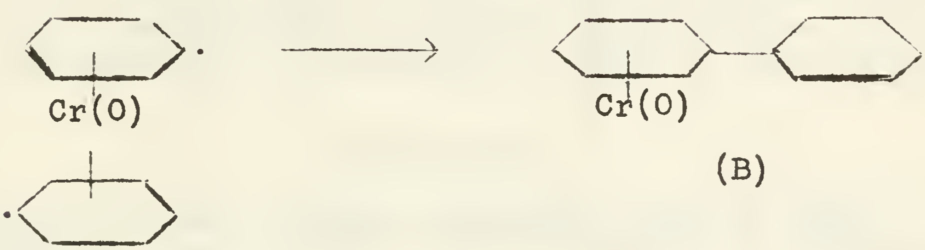
Other investigators have prepared σ-bonded compounds recently by using coordinated ligands that alter the energy of the d electrons (17,18,19). These compounds and their preparation were discussed at a previous seminar.

Recently Zeiss and others (20-24) have reported some interesting work with chromium compounds. The compounds described earlier by Hein were shown to be π-complex compounds. Those compounds decomposed forming biphenyl according to the scheme already described. The first insight into the mechanism of the reaction between ØMgBr and $CrCl_3$ was provided by the isolation of $Ø_3Cr$(III). When this reaction is performed in ether, a black, pyrophoric solid is precipitated. In tetrahydrofuran, however, a red-brown solution results which, upon hydrolysis yields chromium(III) but no π-complex. With a 3-1 excess of ØMgBr, a ppt. of $Ø_3Cr(THF)_3$ is obtained. Removal of tetrahydrofur.n from this red crystalline solid yields a black, pyrophoric solid, which when hydrolyzed yields bis-benzene chromium (0) and benzene biphenyl chromium(0). Hydrolysis in air forms the chromium(I) cations.

Reactions of $CrCl_2$ with ØMgBr in Et_2O at 10°C.

Mole Ratio of $CrCl_2$ to ØMgBr	Time	Product Ratio $Ø_2Cr(0)$ to Ø, Ø-Ø Cr(0)
1:2	2 hr.	3:2
1:2	24 hr.	3:2
1:3	24 hr.	3:2
1:3	4 days	2:3
1:10	4 days	1:9

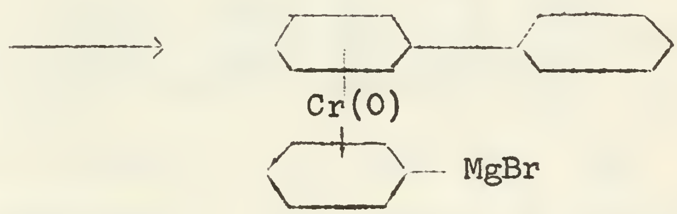
The following mechanism was proposed:



(B)

(A)

(A) or (B)
+ Ø MgBr



(C)

Hydrolysis of these π-complexed intermediates (A or C) or solvolysis with deuterium oxide leads to bis-benzene chromium(0) and benzene biphenyl chromium(0) or the corresponding deuterates. The formation of a nascent form of metallic chromium as the active reducing agent is consistent with these results. The formation of a chromium(I) subhalide is not.

Removal of tetrahydrofuran from the red crystals is not reversible. Thus a drastic change has taken place. Hydrolysis of this isolated intermediate results in the same products and in the same yield as when no intermediates are isolated.

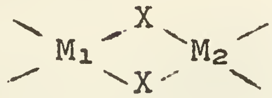
This compound and its congeners have significant potentialities in organic synthesis.

IV. CATALYTIC ACTION OF ALKYL-METAL HALIDE COMPOUNDS

The reaction of transition metal halides with Grignard reagents and other reducing agents is of interest in that these products have catalytic activity in the polymerization of olefins (25-28). These catalysts are generally of the same nature as that described earlier,

that is, black, pyrophoric, and of "uncertain character."

Carrick and others (27) describe these catalysts as being electron defficient:



M_1 = electropositive element (Hl)
M_2 = group IV-VI metal (Ti, V, Cr)

In an effort to find the active site, Carrick and others varied the reducing agent in the presence of vanadium tetrachloride. For all of these reducing agents the activity remained the same. However, using only one reducing agent (triisobutyl aluminum) in the presence of a variety of metal halides, the activity varied, thus indicating the active site to be the transition metal. Further studies along these lines offer broad possibilities in organic synthesis as well as offering a better understanding of transition metals in such systems.

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In an effort to find the active site, [illegible] and others [illegible] [illegible] [illegible] [illegible] to the presence of [illegible] [illegible]. [illegible] of these reducing agents [illegible] [illegible] the same. However, using only the reducing agent ([illegible]) in the presence of a variety of metal halides, the activity varied, thus indicating the active site to be the transition metal. Further studies along these lines offer broad possibilities [illegible] will be [illegible] [illegible] a better understanding of [illegible] [illegible] in such systems.

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COMPLEXES OF RUTHENIUM CONTAINING ONE OR TWO MOLECULES OF PHENANTHROLINE

Harold A. Goodwin May 3, 1960

Bivalent iron, ruthenium and osmium ions all form stable, intensely colored complexes with 1,10-phenanthroline or 2,2'-bipyridine with three base molecules coordinated to the metal ion. These complexes are diamagnetic and their stability is reflected in the ease with which they can be separated into optical isomers.[1]

Basolo and Dwyer[2] have prepared mono and bis-phenanthroline and bipyridine complexes of iron(II) which were found to be paramagnetic. These complexes are unstable in aqueous solution and rearrange to give the corresponding tris complexes and the aquated iron(II) ion. More recently similar complexes of iron(III) have been prepared.[3] These were shown to have magnetic moments corresponding to five unpaired electrons and were unstable in aqueous solution.

Taube[4] has suggested that "the instability of intermediate complexes with respect to disproportionation into extreme forms can be expected for systems in which electron rearrangement takes place at some stage in the series formed by successive substitutions."

Brandt[5] has obtained spectrophotometric evidence for the existence of the species $[Ru\ bipy]^{+++}$ and $[Ru\ (bipy)_2]^{+++}$ in the stepwise addition of bipyridine to ruthenium(III) chloride and was able to isolate $[Ru(bipy)_2(H_2O)_2](ClO_4)_3$.

Dwyer and Gyarfas[6] have found that if tris-(bipyridine) ruthenium (II) chloride is heated *in vacuo* for a long period it loses one molecule of bipyridine and they isolated dark violet dichloro-bis-(bipyridine) ruthenium(II). It was not possible to obtain an analogous phenanthroline complex by this method.

By reacting phenanthroline with potassium pentachloroaquoruthenate(III) under very precise conditions of acidity phenanthrolinium tetrachlorophenanthroline-ruthenate(III), $[phenH][RuCl_4\ phen]$, is obtained. The organic base cation of this salt can be removed by oxidation which yields tetrachlorophenanthroline-ruthenium(IV) and the tetrachlorophenanthroline-ruthenate(III) ion can be regenerated on reduction and isolated as the ammonium salt, $NH_4[RuCl_4\ phen]$. This salt is quite stable and shows no tendency to rearrange to the tris complex in solution. The chloro groups in this complex are labile and can be replaced by a variety of other coordinating groups. However, the phenanthroline molecule is firmly chelated and cannot be replaced.

When $[phen\ H][RuCl_4\ phen]$ is pyrolysed at 300° hydrogen chloride and chlorine are evolved leaving dark violet dichloro-bis-(phenanthroline) ruthenium(II). This is the most convenient method of preparing bis-phenanthroline derivatives of ruthenium. The chloro

groups in [Ru $phen_2$ Cl_2] can be replaced by other coordinating groups but the phenanthroline molecules cannot be replaced and the complex shows no tendency to rearrange to the tris complex.

Both the mono and bis derivatives have magnetic moments corresponding to those expected for low spin octahedral complexes.

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Thesis Report

METAL CHELATES OF SOME POLYAMINOCARBOXYLIC ACIDS AND THEIR HYDROXYETHYL DERIVATIVES

Robert E. Sievers May 10, 1960

During the last 20 years, ethylenediaminetetraacetic acid (EDTA) has been the subject of over 1000 scientific publications.[1] More recently, research interest has shifted to higher analogs of EDTA. One of these, diethylenetriaminepentaacetic acid (DTPA), is particularly interesting because its metal complexes exhibit higher stability than those of EDTA. This increased stability might be explained in several ways. Entropy effects almost certainly play a significant role. It therefore becomes very important to know how many chelate rings have been formed upon complexation.

It has been demonstrated[2-4] that, although EDTA is potentially sexidentate, it may function in a quinque- quadri-, or even bidentate manner. DTPA has eight donor atoms; consequently the structural possibilities of its complexes are much more numerous and complicated. Not only is it potentially octa- or septadentate, but also there are numerous structural possibilities for sexi- and quinquedentate cases.

The infrared technique outlined by Busch and Bailar[2] was employed in this study. This approach makes it possible to detect the presence of uncomplexed -COOH groups by examination of the 1550-1750 cm^{-1} region of the spectra.

The thorium(IV) complex of DTPA was prepared and is formulated as $H[Th(DTPA]\cdot H_2O$. Infrared evidence indicates that in it the ligand is octadentate.

On the basis of potentiometric titrations, earlier workers[5] have proposed that the iron(III) complex of DTPA has either a sexi- or quinquedentate structure. Examination of the infrared spectrum indicates that it is sexidentate, but it is impossible to choose between the various sexidentate structures possible. Study of a ligand which is structurally analogous to DTPA makes it possible to demonstrate whether a particular one of these sexidentate structures is feasible. For this purpose, N,N"-dihydroxyethyldiethylenetriaminetriacetic acid (DDTA) was synthesized and some of its complexes prepared.

The nickel(II) complex of DTPA is either sexi- or quinquedentate. If it is quinquedentate, the choices of structure are limited to one by the spectral evidence.

By reason of their polydentate character, DTPA and triethylenetetraminehexacetic acid (TTHA) form binuclear complexes. The <u>bis</u>-Cu(II), Ni(II) and Mo(V) complexes of DTPA were prepared and their spectra obtained. The spectra of Mo(V) complexes of both DTPA and TTHA indicate that they contain uncoordinated carboxyl groups.

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OBSERVATIONS ON THE RARE EARTHS: STABILITIES OF DIETHYLENETRIAMINEPENTAACETIC ACID CHELATES

Larry C. Thompson May 10, 1960

The factors affecting the stability of chelates have been discussed in general and with particular reference to DTPA. The possibility of the formation of hydrogen and binuclear chelates due to the complexity of the DTPA structure has also been discussed. The methods of determining formation constants and the thermodynamics of chelate formation have been reviewed. The available literature on the quantitative aspects of the formation of rare-earth complexes has been reviewed and the suggested explanations for the gadolinium break have been discussed.

Titration curves have been obtained for DTPA and various mixtures of neodymium and DTPA. These indicated that the reaction between DTPA and the rare-earth ions results in the formation of a one to one chelate and also a chelate containing a hydrogen ion as well as a rare-earth ion.

The DTPA has been titrated electrometrically under carefully controlled conditions at 10°C., 20°C., 30°C., and 40°C. The values of the acid dissociation constants obtained at 20°C. agree well with the values in the literature. The values of pK_3, pK_4 and pK_5 have been treated by a least square analysis and the corresponding values of ΔF^o, ΔH^o, and ΔS^o have been determined at 25°C. These values have been compared with the corresponding values for EDTA. It has been shown that the fourth and fifth dissociation steps of DTPA are very similar.

The dissociation constants of the mercury(II)- and rare-earth-hydrogen-DTPA chelates have been determined by a pH method. The proton is undoubtedly on a carboxyl group in the rare earth chelates, but the position of the proton in the mercury(II) chelate is not clear.

The mercury-indicator electrode has been used to determine the formation constants of the mercury(II)- and rare earth- DTPA chelates as a function of temperature. The data have been treated by a least squares analysis and the values of ΔF^{o}, ΔH^{o}, and ΔS^{o} have been determined for the formation of the chelates. The values of the formation constants have been compared with the values in the literature and reasons for considering these new values as the more accurate are advanced. The formation constants and thermodynamic values have been compared with comparable values for other rare-earth chelates and possible explanations for the observed trends have been suggested.

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THESIS REPORT

SUBSTITUTION REACTIONS OF CIS-DICHLORO-(β,β',β'' TRIAMINOTRIETHYLAMINE)-COBALT(III) COMPLEX ION.

I. Kinetics of Aquation of cis-Dichloro-(triaminotriethylamine)-Cobalt(III) Ion under Various Conditions.

II. Kinetics of Base Hydrolysis of cis-Dichloro-(triaminotriethylamine)-Cobalt(III) Ion under Various Conditions.

III. Kinetics of Reaction of cis-Chloronitro-(triaminotriethylamine)-Cobalt(III) and the Aquonitro-(triaminotriethylamine)-Cobalt(III) Ions with Nitrite, Azide and Thiocyanate Ions in Aqueous Media.

Stanley K. Madan May 17, 1960

Basolo (1) has pointed out that stereochemical properties are not sufficient to define the reaction mechanisms of hexacovalent complexes and that it is essential to use both kinetic and stereochemical data in any attempt to elucidate the mechanisms of these reactions.

It is further pointed out by Taube (2) that although the radius of the central ion, its charge, the nature of the attached groups, and the bond type are all important factors in determining a rate of substitution, fixing these (and the experimental conditions) does not fix the rate.

This work was undertaken for the purpose of exploring the relation between ligands which give complexes of fixed configuration and the kinetics of substitution in these complexes. The initial objective of this work, therefore, was to prepare compounds of cobalt(III) having fixed geometrical configurations--namely, those of trans-dichloro-(tetrapyridyl)-cobalt(III) and cis-dichloro-(triaminotriethylamine)-cobalt(III) ions, and then to compare the kinetics of some reactions of these complexes.

Part I. In this part the syntheses of these ligands and their respective compounds are reported. Tetrapyridyl was synthesized from pyridine, which was converted to dipyridyl by the use of activated Raney-Nickel. The dipyridyl was then subjected to a vapor phase reaction in a sealed tube at 310°C for four hours. Iodine was used as an oxidizing agent. The resulting mixture of unreacted dipyridyl and the tetrapyridyl which had been formed was separated by a chromotographic technique using activated alumina.

However, the comparison of the kinetics of reactions of these compounds had to be abandoned because the tetrapyridyl cobalt(III) complex was found to aquate very rapidly, which made it impossible to obtain accurate measurements.

[illegible]

[illegible]

I. [illegible] for [illegible] under Various Conditions.

II. [illegible] under Various Conditions.

III. [illegible] in Aqueous Media.

[illegible] May 17, 1950

[illegible]

[illegible]

[illegible]

Part I. [illegible]

[illegible]

It was decided, therefore, to make more detailed kinetic investigation of the reactions of cis-[Co tren $Cl_2]^+$. The triaminotriethylamine ligand provides a tertiary nitrogen atom trans to one chloro group and also imparts a fixed cis configuration to the cobalt(III) complex. The study of the kinetics of the acid hydrolysis of cis-[Co tren $Cl_2]^+$ at pH 1.0, under various conditions of added electrolytes and at three different temperatures, was conducted. A chloride concentration cell was employed to measure the rate of chloride release. The pseudo-first-order constant for the loss of one chloride ion is given by $k_1=8.80 \times 10^{-4} sec^{-1}$ and $E_a=6 \cdot 5$ k.cal. A value for the specific rate constant for the loss of a second chloride ion has been estimated. The effects of certain salt additions have been interpreted as support for an S_N1 mechanism. In some cases, a slight change in specific rate constant with initial concentration of the complex has been observed, and the overall rate has been found to be proportional to the concentration. A possible explanation for this behavior is presented. The higher value of the specific rate constant k_1, as compared to that of acid hydrolysis of similar ions, such as cis-[Co en_2 $Cl_2]^+$ and cis-[Co trien $Cl_2]^+$, which follow the same mechanism, is justified by a suitable explanation. The possibility of inductive effects of the ligand as a cause of the weakening of the Co-Cl bond, or alternatively the trans-effect, due to the poor coordinating ability of the tertiary nitrogen atom, is suggested.

Part II presents the results of kinetic measurements of base hydrolysis of the cis-dichloro-(triaminotriethylamine)-cobalt(III) ion under various conditions. This being a very fast reaction, measurements were made at only one temperature, i.e., 0.1°C. A conductivity cell in circuit with a three-frequency oscillator, three-frequency tuned amplifier, Campbell Shackleton Ratio Box, and oscilloscope detector was employed to measure the rate of chloride ion formation. An overall second-order kinetics was observed for the replacement of the chloro group, and first-order with respect to the concentrations of each reactant. The second-order rate constant for the loss of one chloride ion is given by $k_1=0.55 \times 10^2 M^{-1} sec^{-1}$. The kinetic measurements indicate, with one equivalent of complex and one of base, that the reaction proceeds as follows:

$$\text{cis-[Co tren } Cl_2]^+ + OH^- \longrightarrow \text{cis-[Co tren } Cl(OH)]^+ + Cl^-$$
$$\text{cis-[Co tren } Cl(OH)]^+ + H_2O \longrightarrow \text{cis-[Co tren } H_2O(OH)]^{++} + Cl^-$$

When one equivalent of complex is used to two equivalents of base, the reaction proceeds in the same manner, both chloro groups being replaced stepwise by hydroxyl groups.

Part III deals with the study of reactions of cis-chloronitro-(triaminotrethylamine)-cobalt(III) ions with azide, nitrite, and thiocyanate ions in aqueous media. Spectrophotometric and potentiometric methods were utilized to study the kinetics of these reactions.

The results of measurements indicate that there is a good agreement between rates of chloride ion formation in the absence and in the presence of varying amounts of nitrite and azide ions. This supports the belief that the replacement of groups from this complex ion proceeds through an intermediate aquation reaction, the rate of which is independent of the concentration of the ion which is entering the complex. With thiocyanate ion, a first-order plot was not obtained, probably due to ion-pair formation. The same effect was observed in the reaction of cis-aquonitro-(triaminotriethylamine)-cobalt(III) ion with thiocyanate.

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Thesis Report

POLARIZED CRYSTAL SPECTRA OF TRIVALENT VANADIUM AND CHROMIUM

Richard L. Carlin May 17, 1960

The substance $NaMgAl(C_2O_4)_3 \cdot 8H_2O$ crystallizes in the rhombohedral crystal system and contains two molecules in the unit cell. The molecular axis of the trigonally distorted trisoxalato-aluminate (III) ion coincides with the sixfold axis of the prismatic single crystal. Thus, one may observe the absorption spectrum of this crystal in three ways: with the light beam along the crystal axis or normal to it (two polarizations).

Single crystals of this material have been grown by several techniques from aqueous solutions, with a certain amount of the aluminum isomorphously replaced by either trivalent vanadium or chromium. Visible spectra of these crystals have been observed both at room temperature and at liquid nitrogen temperature.

Two types of bands are observed with each metal, those broad bands which are caused by electronic transitions between levels of the same multiplicity and the narrow lines of the spin-forbidden transitions. From an analysis of these spectra, the following results have been obtained:

(1). The first excited doublet level of chromic ion has been assigned. In contrast to the case with ruby, the splitting of the degeneracy by spin-orbit coupling is not observed.

(2). The next higher spin-forbidden level of chromic ion has also been tentatively assigned.

(3). The spin-allowed levels of chromic ion follow the selection rules for polarized light remarkably well. These rules are based simply on the symmetries of the orbital levels involved and thus show that a static distortion may be all that is necessary to remove the d-/-d selection rule. Vibrational perturbation is then not necessary in order to explain the intensities.

(4). The spin-allowed bands of vanadic ion also follow the selection rules and have allowed the assignment of the energy levels.

(5). Vanadium(III) has a single spin-forbidden line in the 20,500 wave number region. By observing the various polarized spectra, it has been unambiguously shown, contrary to expectation, that this line is caused by an electric dipole transition.

THESIS REPORT

COORDINATION COMPOUNDS WITH A PHOSPHITE ESTER

John G. Verkade May 24, 1960

Many phosphite esters (i.e., $(RO)_3P$) (1) have been prepared and characterized as well as some of their coordination compounds formed with salts of metals such as copper, silver, gold, platinum, and mercury (2). Many of these complexes are stable and some of them exist as dimers and trimers (2). It has also been found that attempts to prepare coordination compounds of salts of metals such as cobalt, iron, nickel, tin, and lead with some of the lower trialkyl phosphites resulted only in intractable syrups (2).

In this research a ligand (I) having minimal steric hindrance and hence reduced ligand-ligand repulsion in the complex was designed. This ligand was synthesized by the reaction (3):

$$PCl_3 + \left.\begin{matrix}HOCH_2\\HOCH_2\\HOCH_2\end{matrix}\right> CCH_3 + 3\ \text{pyridine} \xrightarrow{THF} P\left<\begin{matrix}OCH_2\\OCH_2\\OCH_2\end{matrix}\right> CCH_3 + 3\ \text{pyridinium hydrochloride}$$

I

Many monocyclic phosphite esters (e.g., $CH_2CH_2CH_2OPO(OR)$) (4) have been prepared but only one other fully constrained structure has been characterized (II) (5). Scale models reveal, however, that I is less

II

strained and less bulky than II.

The characterization of I was carried out by infrared, proton nmr, phosphorus nmr, molecular weight, and dipole moment studies. It is interesting to note that the dipole moment of I is more than twice that of $P(OEt)_3$.

Coordination compounds of various transition metals with I were prepared by adding I to alcoholic solutions of metal salts. These were characterized by means of magnetic susceptibility measurements, conductivity studies, molecular weight determination, infrared, ultraviolet, and visible spectral studies, phosphorus nmr, microscopy, and

polarographic data. The metal ions which formed isolable compounds included cobalt(I), cobalt(II), cobalt(III), copper(I), nickel(II), platinum(II), palladium(II), silver(I), and rhodium(III).

The first-row transition-metal complexes of I in keeping with the low steric hindrance of the ligand usually attain their maximum coordination numbers with only the phosphite in the first coordination sphere: CoI_5^{+}, CoI_4^{+2}, CoI_6^{+3}, CuI_4^{+}, NiI_4^{+2} and AgI_4^{+}. That I exerts an unusually strong field is supported by the fact that the cobalt(III) compound is completely colorless and exhibits no visible or ultra-violet absorption band. No other cobalt(III) complex known is colorless.

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THESIS REPORT

MOLECULAR ADDITION COMPOUNDS OF IODINE

Norman J. Rose May 24, 1960

That iodine is establishing itself as a reference acid in several nonaqueous solvents is clearly indicated by the volume of work in this area.[1] In CCl_4 solutions, iodine and various Lewis bases (B) generally follow the stoichiometry represented by the following equation:

$$I_2 + B = BI_2 \tag{1}$$

Because of the solubility of all the species in CCl_4, crystal lattice effects and extensive solvation are absent. The systems are conveniently studied spectrophotometrically because three separate regions are available for investigation: (1) the free iodine peak (5150 Å) and (2) the two peaks characteristic of the complex. These occur at 4600 Å and at 2600 Å when the base is N,N-dimethylacetamide (DMA).

The mathematical interpretation used in this study to obtain equilibrium constants from the spectral data[2] may be derived from the equilibrium constant expression for equation (1) and an expression for the absorbance due to the three species present at any wavelength.

$$K^{-1} = -\left(C_B + C_I\right) + \frac{A - A^o_I - A^o_B}{e_c - e_b - e_i} + \frac{C_B C_I (e_c - e_b - e_i)}{A - A^o_I - A^o_B} \tag{2}$$

where: C values = initial concentrations
A values = absorbance at any wavelength
e values = extinction coefficients
$A^o_I = e_i C_I$ $A^o_B = e_b C_B$

K^{-1} = reciprocal of equilibrium constant

If it is known that a species does not absorb at the wavelength under consideration, the appropriate value in the equation is ignored. Ideally, lines made by plotting K^{-1} versus selected $e_c - e_i - e_b$ terms for various C_B and C_I values have a common intersection, one of the co-ordinates of which is K^{-1} for the system. A thermostat constructed for the Cary Model 14 recording spectrophotometer provided a means for obtaining the spectra at various temperatures.

The thermodynamic entities available from the lnK versus 1/T relationship were determined for the DWA-I_2 system.

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